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Balancing from FRET to SET and Further to Photochemistry

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Dedication to Prof. Niyazi Serdar Sariciftci on the occasion of his 60th birthday.

Abstract: Dyads of the hypsochromically absorbing energy donor benzoperylenetriscarboximide and the more bathochromically absorbing perylenebiscarboximide with various spacers were synthesized by means of the Sonogashira reaction where the transition moments of the donor and the acceptor are orthogonal causing zero for the geometry factor of κ for the simple *p*-phenylene spacer. Exciton interactions were extinguished; however, the energy transfer by RET (resonance energy transfer) proceeded unaltered efficiently in contrast to the theory where vibronic effects were made responsible therefore. A lateral shift of donor and acceptor by means of a disubstituted naphthalene as the spacer was of no influence. The replacement of the naphthalene by the more electron rich pyrene caused a switch from RET to a photo-induced single electron transfer (SET). RET as a very fast feeder allowed the suppression the formation of triplets of the donor and subsequent the generation of singlet oxygen and allowed to protect the dyad against photochemical degradation. Finally, the influence of the distance between donor and acceptor was studied.

Keywords: SET · FRET · Photochemistry · Fluorescence · Perylenes

1. Introduction

Solar radiation is a nearly unlimited energy source concerning human needs; however, its low energy density efforts special procedures.[1] Light collection on a molecular level[2] proceeds in the natural[3] photosynthesis reaction centres[4] and is finished by electron transfer reactions[5] to obtain chemically stored energy. The transport of energy from an energy donor (*D*) to an acceptor (*A*) with no direct contact of orbitals[6] is commonly attributed to an electrodynamic interaction[7] of the involved transition dipoles where Förster's popular mechanism[8] of resonance energy transfer (FRET) resulted in two chemicals important structural parameters[9] influencing the rate constant of such a process: (i) the R^{-6} dependence of the distance between the centres of the dipoles and (ii) the orientation factor κ of the dipoles according to eq. (1).[10]

$$\kappa = \cos(\theta_T) - 3\cos(\theta_D)\cos(\theta_A) \quad (1)$$

θ_T in eq. (1) means the angle between the transition moments of the donor (*D*) and acceptor (*A*) and the angle θ_D between the donor transition moment and the interconnecting vector. The angle θ_A is the analogous angle of the acceptor. However, there were doubts[11] concerning the general validity of Förster's theory for real systems because the energy transfer proceeded unexpectedly unrestricted between systems with orthogonal arrangements[12,13] and $\kappa = 0$ for the molecular graph; molecular vibrations were made responsible[14] for the process of energy transfer. On the other hand, exciton interactions of such proximate chromophores are uncoupled[15] in these orthogonal arrangements allowing the study of energy and electron transfer independently of other interactions. Benzoperylenetriscarboximides (compare **3** in Scheme 1, below) and perylenebiscarboximides (compare **1** in Scheme 1) are suitable[16] for the construction of model compounds with aromatic spacers and are here applied for the study of energy transfer and the gradual shift to electron transfer because of the special geometry.

2. Results and Discussion

The chromophores are targeted to be well separated from the linking position by aryl groups where the Sonogashira[17] reaction allows an efficient coupling to ethynyl-substituted spacers. Following this concept, we firstly prepared a reference material with a simple *p*-phenylene as a spacer according to Scheme 1. The long-chain secondary alkyl group (swallow-tail substituent) 7-tridecyl in the perylenebiscarboximide[18] **1** mediates sufficiently high solubility both for the starting materials and the reaction products.

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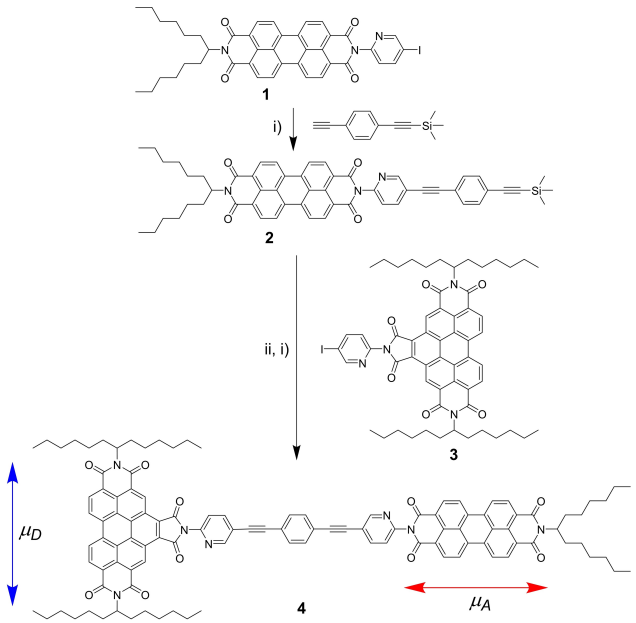


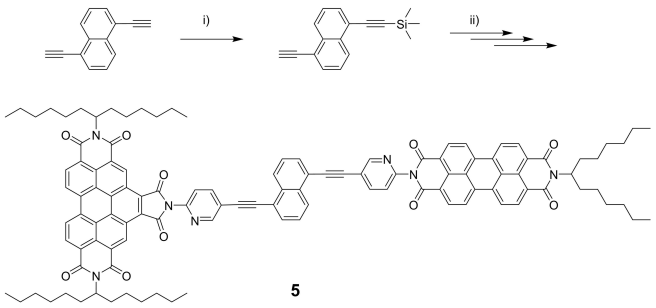
Scheme 1. Synthesis of **4**; i) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3 THF/TEA, 80 °C bath, 16 h, 54 % for **2** and 41 % for **4**, ii) TBAF, THF, 59 %. Transition moment μ_D of the donor (blue) and of the acceptor μ_A (red).

The iodine atom in **1** allows a C–C-coupling by means of the Sonogashira reaction. A simple carbocyclic phenyl substituent would be attractive; however, the group becomes sufficiently electron rich for electron transfer to the electronically excited chromophor if substituted with ethynyl groups[12b] in the target compounds and interferes the subsequent investigations. As a consequence, we replaced the phenyl group by the heterocyclic pyridyl group with a more electron depleated heteroaromatic system to obtain **1**. Semi-protected bis-*p*-ethynylbenzene[19] by means of a trimetylsilyl group[20] was allowed to react with the latter in a Sonogashira reaction to obtain **2**; see Scheme 1. Deprotection with tetrabutylammoniumfluoride (TBAF) and a subsequent Sonogashira reaction with **3** allowed the synthesis of the dyad **4**. The transition moments in **4** were subsequently laterally shifted to obtain a skew-oriented arrangement.

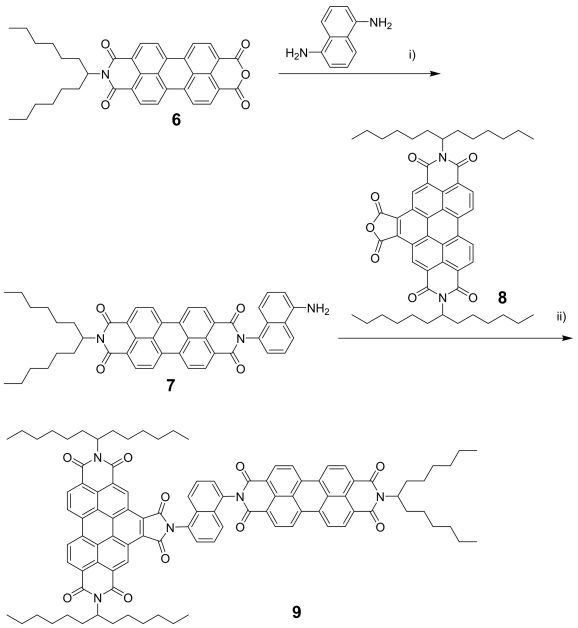
Naphthalene was applied as a spacer for the lateral shift of the chromophores where 1,5-bisethynylnaphthalene[21] was semi-protected by deprotonation with the ethyl Grignard reagent and silylation with trimethylsilylchloride (TMSCl) by means of the method described by Ghose;[20] see Scheme 2. The subsequent steps comprising the coupling with **1**, deprotection and coupling with **3**, followed exactly the methods described in Scheme 1 to obtain **5**.

The spacer was shortened for an increased skew lateral shift; thus, 1,5-diaminonaphthalene was condensed with the anhydride **6** to obtain the component **7** where melt imidazole favored the mono condensation. **7** was further condensed with **8** in quinoline to obtain the dyad **9**; see Scheme 3.

The aromatic spacer of the latter was further extended to pyrene. Thus, 1,6-diaminopyrene was analogously condensed

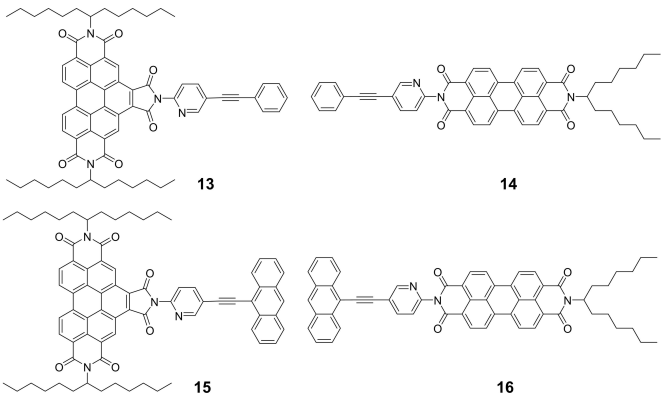


Scheme 2. Synthesis of **5**; i) EtMgBr in THF, TMSCl; ii) **1**, Pd-$(PPh_3)_2Cl_2$, CuI, PPh_3 THF/TEA, 80 °C bath, 3 h, 48 %; TBAF, THF; **3**, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3 THF/TEA, 80 °C bath, 6 h, 50 %.



Scheme 3. Synthesis of **9**; i) imidazole, 150 °C, 3 h, 77 %; ii) quinoline, 150 °C, 20 h, 21 %.

with **6** to the intermediate **11** and further with **8** to obtain the dyad **12**; see Scheme 4.



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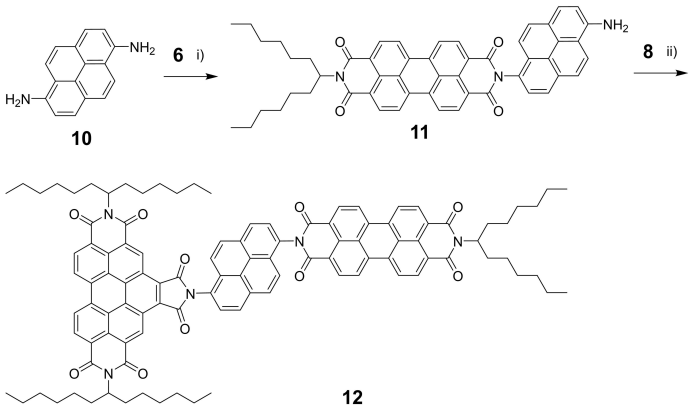

Scheme 4. Synthesis of **12**; i) imidazole, 150 °C, 3 h, 76%; ii) quinoline, 150 °C, 18 h, 7%.

Finally, compounds **13** and **14** were prepared as reference materials for the donor and the acceptor with spacers ending at phenyl groups and **15** and **16** for spacers ending at anthracenyl groups as models for more extended aromatics in spacers.

The UV/Vis absorption spectrum of **4** is the sum of the spectra of the components as is shown in Figure 1 by the comparison with the donor represented by **13** and the acceptor represented by **14**; orbital nodes[22] in HOMO and LUMO of perylenebiscarboximides allow the decoupling of the chromophores in **4** and can also exclude an energy transfer through bond (TNET).[23] The orthogonal arrangement of the transition moments in **4** (blue and red vectors in Scheme 1) extinguishes[15] exciton effects so that there is no interference concerning the additivity of the spectra. An electronic excitation of the acceptor at 491 nm induces its strong fluorescence with a quantum yield close to unity where the fluorescence spectrum is identical with the spectrum of **14** as the model compound (Table 1). On the other hand, an optical excitation of the donor at 437 nm indicates its complete fluorescence quenching because emission would be expected below 500 nm; see the red curve in Figure 1. Instead, a strong fluorescence of the acceptor is observed (red curve above 500 nm) where a fluorescence quantum yield of 93% is found indicating a complete energy transfer from the donor to the acceptor with a maximal efficiency indicated by the observed high quantum yield. This experimental result is remarkable because Förster's theory postulates the interrupting of the energy transfer for $\kappa = 0$ as is given by the orthogonality of the transition moments. This results corresponds to prior observations[12] (see an independent verification[13]) and is attributed to the contribution of vibrations.[14] An intermolecular energy transfer as competing process could be excluded because of the high dilution where the probability for a molecular contact or approximation becomes very low. For example, the dyad **5** was excited at 437 nm and a molar absorptivity of 44000 at an optical density of 0.007 for a path of 1 cm. Thus, the molar concentration was $1.6 \cdot 10^{-7}$ where each molecule moves in a cube of 220 nm lengths and the calculated[24] mean intermolecular distance is 120 nm.

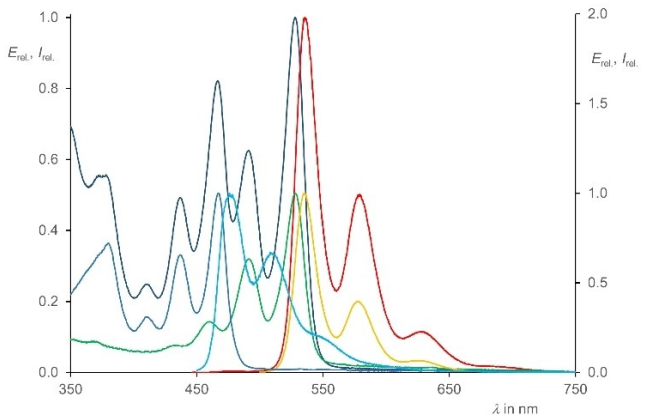

Figure 1. Normalized UV/Vis spectra in chloroform. Dark blue: Absorption spectrum of **4** (left scale E_{rel}), violet: Absorption spectrum of **13** (right scale), green: Absorption spectrum of **14** (right scale E_{rel}), red: Fluorescence spectrum of **4** (left scale I_{rel}, optical excitation of the donor at $\lambda_{exc} = 437$ nm), light blue: fluorescence spectrum of **13** (right scale), yellowish orange: Fluorescence spectrum of **14**.

The chromophores in **4** are linearly T-like arranged in line so that the direction of the transition moment of the acceptor orthogonally hits the centre of the vector of the donor. We shifted the vector of the acceptor in **5** laterally into a skew position and investigated the influence on the spectra. Moreover, the spacer is no more linear, but staggered in zigzag; this may influence longitudinal and transversal oscillations of the spacer. The absorption spectrum of **5** remains unaltered the sum of the individual chromophores (Figure 2). The fluorescence quantum yield of the irradiated acceptor at 591 nm remains close to unity whereas the fluorescence of the donor irradiated at 437 nm is completely quenched by the energy transfer to the acceptor indicated by a fluorescence quantum yield of 92% of the latter. As a consequence, neither a skew arrangement of the chromophores nor a staggered zigzag spacer is of any influence on the energy transfer.

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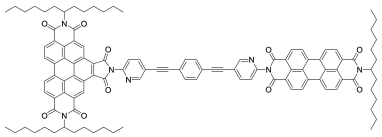
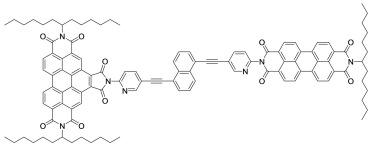
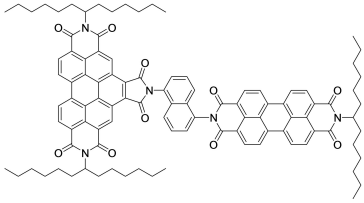
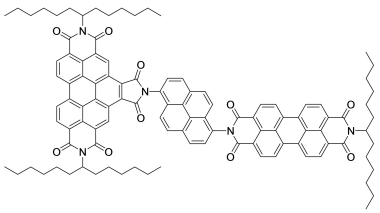
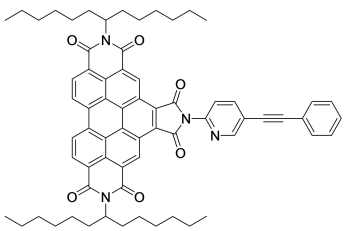
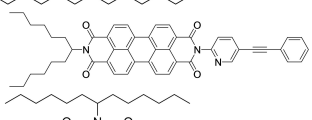
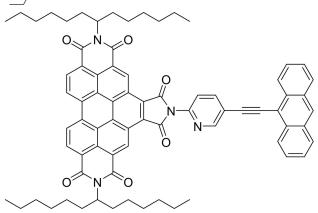
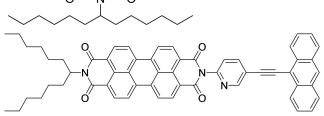
Table 1. Fluorescence quantum yields of dyads for optical excitation of the donors ($\Phi_{436\,nm}$) and the acceptors ($\Phi_{491\,nm}$) compared with isolated donors and acceptors.

	Compound	Φ_{436}	Φ_{491}
4		0.93	1.00
5		0.92	1.00
9		0.98	1.00
12		< 0.01	< 0.01
13		0.014	–
14		–	1.00
15		photo labile	–
16		–	< 0.01

A further skew displacement of the transition moments was obtained by the shortening the spacer in **9** where the electronical decoupling of donor and acceptor was still maintained by orbital nodes[22] in the HOMO and LUMO of the linking nitrogen atom of the acceptor. The absorption spectrum remained still the sum of components as is shown in Figure 3. A fluorescence quantum yield of close to unity was

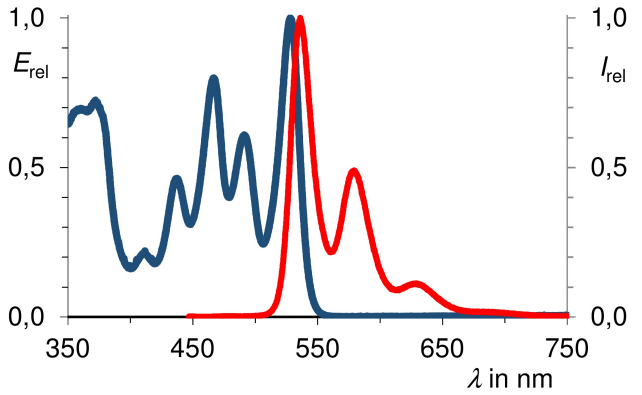


Figure 2. Normalized UV/Vis spectra of **5** in chloroform. Left: Absorption spectrum, right: Fluorescence spectrum (left scale, optical excitation of the donor at $\lambda_{exc} = 437$ nm).

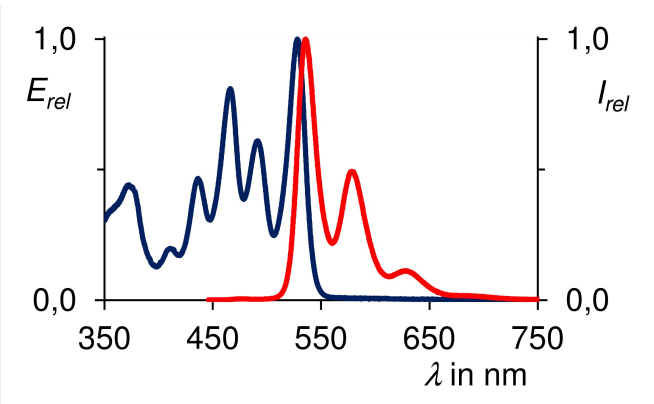


Figure 3. Normalized UV/Vis spectra of **9** in chloroform. Blue: Absorption spectrum (left scale), red: Fluorescence spectrum (right scale, optical excitation of the donor at $\lambda_{exc} = 437$ nm).

obtained for the excitation of the acceptor at 491 nm. The fluorescence of the donor for the excitation at 437 nm is completely quenched by an efficient energy transfer to the acceptor indicated by a fluorescence quantum yield of 98% of the latter. The slightly different quantum yields for the energy transfer in **4**, **5** and **9** might be caused by different photophysical processes; however, they are close to experimental uncertainties and are not further discussed here.

The aromatic system of the spacer was extended to pyrene in the dyad **12**. The UV/Vis absorption spectrum in the visible is still the sum of the spectra of donor and acceptor; see Figure 4. However, no fluorescence of **12** is found; an extension of the aromatic system of the spacer to pyrene increases the electron-donating properties and causes quenching by SET; compare.[12b]

The light absorption of perylene dyes such as **14** proceed between comparably pure π-orbitals (HOMO, LUMO) both in absorption and fluorescence with a quantum yield of close to unity for the latter. This remains unaltered if the HOMO of attached aromatic systems of spacers are below the HOMO of

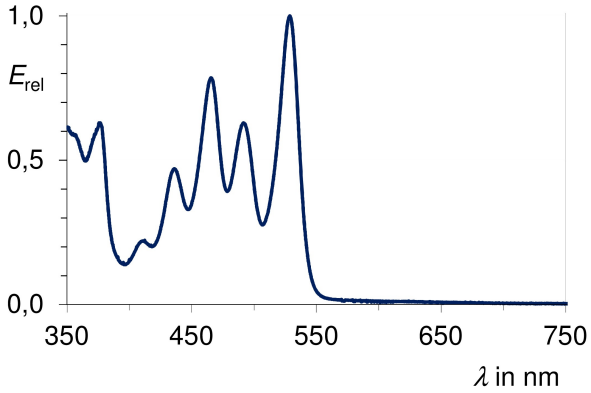


Figure 4. Normalized UV/Vis spectrum of **12** in chloroform.

the perylene chromophore as is given in **4**, **5**, **9** and **14** where high fluorescence quantum yields are observed. However, the HOMO of the electron rich spacer in **12** is higher than the HOMO of the chromophore; see Figure 5, left. An electronic excitation of the chromophore generates an electron hole in the HOMO; this can be filled by an electron transfer (SET) from the spacer; see Figure 5, middle. Thus, fluorescence becomes blocked because of the completely filled HOMO of the chromophore; see Figure 5, right. As a consequence, fluorescence is quenched and SET can be applied for charge transfer; for similar processes see refs..[25,26] This process is coupled with energy transfer (RET) in the dyad **12** where even light energy absorbed by the donor is transferred to the acceptor and ended up in SET. Thus, such dyads as **12** can be applied as broadband light absorbers for finally efficient photo-induced SET (PET).

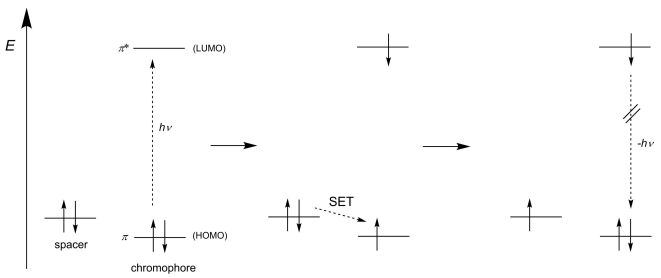
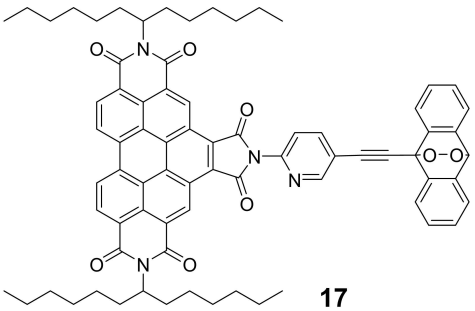


Figure 5. Schematic photo-induced electron transfer (SET) from a spacer with energetically high-lying orbitals (*E*): (i) Electronic excitation of the chromophore (*hν*), (ii) electron transfer (SET) from the spacer filling the half-occupied orbital, (iii) blocked fluorescence because of the filled HOMO.



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Furthermore, we studied the SET with the two isolated chromophores of the dyad **12** with attached anthracene for simulating electron rich spacers. Thus, the model compound **16** characterizing the acceptor gave the typical structured absorption spectrum of perylene dyes such as **14**. However, fluorescence was completely quenched indicating an efficient SET mechanism from the attached anthracene to the chromophore according to Figure 5. Dye **16** is very photostable in spite of the light-induced processes generating radical cations and radical anions; this may be caused by the high stability of such perylene radical anions[27] and furthermore the low tendency for the generation of triplet states and the subsequent formation of singlet oxygen for oxidative degradation. The model compound **15** for the donor gave the typical UV/Vis absorption of benzoperylenetriscarboximides such as **13**. Fluorescence is also quenched indicating a similar process as for **16**; however, **15** is photo labile and becomes photo oxidized to form the fluorescent **17**. Benzoperylenetriscarboximides are known for their tendency to undergo inter system crossing (ISC) to form their triplet states[28] and the formation of singlet oxygen[29] by sensibilisation. The latter reacts in a Diels Alder reaction to form the endoperoxide **17** indicated by its mass spectrum. The aromatic system of the anthracene in **17** becomes interrupted and is no more electron rich enough for SET; as a consequence, **17** is fluorescent in contrast to **15**. Obviously, the ISC in **15** can compete with SET. On the other hand, the dyad **12** is very photostable where no oxidative photodegradation was observed. This is interpreted in terms of a very fast RET from the donor to the acceptor so that there is not enough time left for the photo-exited donor to undergo ISC. As a consequence, RET protects **12** versus photodegradation. The tendency of the finally excited perylenebiscarboximide as acceptor in **12** to undergo ISC and the subsequent generation of the oxidizing and thus degrading singlet oxygen is very low so that finally only SET proceeds.

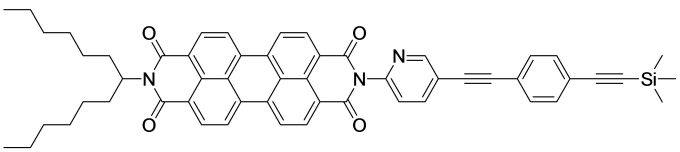
3. Summary

Dyads of benzoperylenetriscarboximides as energy donors and perylenebiscarboximides as energy acceptors could be efficiently synthesized by means of the Sonogashira cross coupling and condensation reactions, respectively. Orthogonal transition moments in a T-like arrangement of donor and

acceptor extinguished exciton interactions leaving the UV/Vis spectra of the components unaltered and the spectra of the dyad the sum of its individual chromophores. Resonance energy transfer (RET) proceeded efficietly in such a dyad with T-arranged orthogonal transition moments in contrast to Förster's theory of energy transfer (FRET) predicting an inhibition of the energy transfer because the geometry factor κ becomes zero. A lateral shift of the transition moments to become skew-arranged did not influence the energy transfer; the latter is attributed to proceed by molecular vibrations; this may be specified as vibration-induced resonance energy transfer (VRET). An increase of the electron density of the spacer in the extended aromatic pyrene caused a switch to photo-induced electron transfer (SET and PET, respectively) with fluorescence quenching. An investigation of the individual chomophores in such a process indicated that the stability of perylenebiscarboximide (acceptor) remains unaffected, whereas the benzoperylenentriscarboximide (donor) generates singlet oxygen by means of ISC (inter system crossing) degrading the dye. The high photostability of the dyad **12** indicates a stabilizing effect of the dyad by FRET because ISC of the donor is suppressed by the fast competing energy transfer to the acceptor. This is estimated to be important for the construction of light-collecting and light-harvesting complexes.

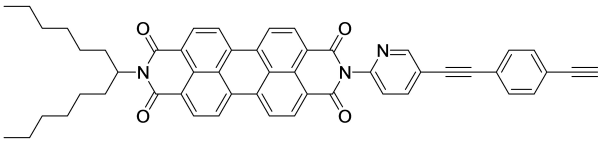
4. Experimental Section

General Information. Available standard chemicals were applied in synthesis grade without further purification. Chloroform was used in spectrophotometric grade. Yields refer to the isolated compounds estimated to be > 95% pure as determined by ^{1}H NMR (25 °C); all dyes were uniform according to T.L.C.. Chemical shifts are reported as δ values in ppm calibrated with the solvent peak. NMR spectra were recorded in the solution of $CDCl_3$ (residual chloroform: $\delta = 7.27$ ppm for ^{1}H NMR and $\delta = 77.0$ ppm for $^{13}C\{^1H\}$ NMR). Abbreviations for signal coupling are as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sxt, sextet; and m, multiplet. Infrared spectra were recorded from 4000–400 cm^{-1} on a Perkin 281 IR spectrometer. Samples were measured neat (ATR, Smiths Detection Dura Sample IR II Diamond ATR). The absorption bands were reported in wave numbers (cm^{-1}). Mass spectra were recorded on a Finnigan MAT 95Q or Finnigan MAT 90 instrument for electron impact ionization (EI) with direct vaporization of the sample (DEP/EI) from a platinum fiber 20 until 1600 °C at 60 °C·min^{-1}. High-resolution mass spectra (HRMS) were recorded on the same instrument. UV-Vis spectra were obtained with a Varian Cary5000 spectrometer. Fluorescence spectra were obtained with a Varian Cary Eclipse spectrometer, slit width 2.5 nm. Column chromatography was performed using SiO_2 (0.040–0.063 mm, 230–400 mesh ASTM) from Merck if not indicated. Fluorescence quantum yields were determined analogously to ref.[30] by means of the standard **S-13** (CAS RN 110590–84-6; chemical name: 2,9-bis-(7-tridecyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone) or **C-25**[31] (CAS RN 335458-21-4; chemical name: 2,10-bis(1-hexylheptyl)-6-[2-[3,8,9,10-tetrahydro-9-(1-octylnonyl)-1,3,8,10-tetraoxoanthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinolin-2(1*H*)-yl]ethyl]-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone). The interpretation of NMR signals was verified with carbon-proton (HMBC) and proton-proton (COSY, NOESY) correlation methods. All reagents were obtained from commercial sources and used without further purification if not otherwise stated.

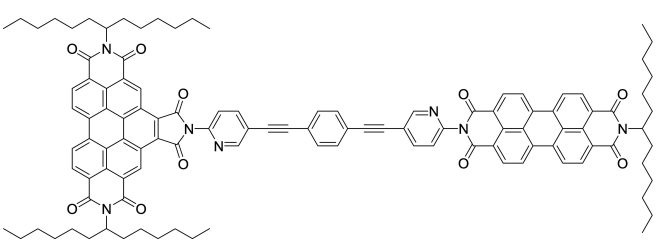


2-(1-Hexylheptyl)-9-[5-(4-trimethylsilanylethynylphenylethynyl)-pyridin-2-yl]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (2): *N,N‴*-Bis(1-hexylheptyl)-*N′*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1′,2′:3,4:9,10-hexacarboxylic-1′,2′:3,4:9,10-tris (dicarboximide) (**1**, 150 mg, 194 µmol) under argon atmosphere was dissolved in THF (6.0 mL), treated with $PdCl_2(PPh_3)_2$ (13 mg, 19 µmol), CuI (4.8 mg, 25 µmol), PPh_3 (5.0 mg, 19 µmol), then treated with (4-ethynylphenylethynyl) trimethylsilane (46 mg, 0.23 mmol), triethylamine (3.0 mL), stirred at 80 °C (bath) for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 800 × 44 mm, chloroform/ethanol 60 : 1). Yield 88 mg (54%) red solid, m.p. > 250. R_f-value (chloroform/ethanol 60 : 1) = 0.30. IR (ATR): $\tilde{\nu}$ = 2954.3 (w), 2922.3 (w), 2855.7 (w), 2361.0 (w), 2335.1 (w), 2155.8 (w), 1706.5 (m), 1693.0 (s), 1664.4 (s), 1652.9 (s), 1591.3 (s), 1577.1 (m), 1501.7 (w), 1477.1 (w), 1432.0 (w), 1403.4 (m), 1339.7 (s), 1248.7 (s), 1174.3 (m), 1138.3 (w), 1125.5 (w), 1105.5 (w), 1030.4 (w), 965.9 (w), 859.3 (s), 841.1 (s), 810.1 (s), 745.0 (m), 721.0 (w), 690.6 (w), 667.6 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.27 (s, 9 H, $Si(CH_3)_3$), 0.83 (t, ^3J(H,H) = 7.1 Hz, 6 H, 2 × CH_3), 1.18–1.38 (m, 16 H, 8 × CH_2), 1.84–1.91 (m, 2 H, β-CH_2), 2.21–2.28 (m, 2 H, β-CH_2), 5.16–5.21 (m, 1 H, N–CH), 7.45 (d, ^3J(H,H) = 8.1 Hz, 1 H, $CH_{pyridine}$), 7.47–7.54 (m, 4 H, 4 × $CH_{aromat.}$), 8.06 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.62–8.73 (m, 8 H, 8 × $CH_{perylene}$), 8.87 ppm (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 0.1, 14.0, 22.6, 26.9, 29.2, 31.7, 32.4, 54.8, 87.0, 93.3, 96.8, 104.4, 121.0, 122.3, 123.0, 123.1, 123.4, 123.8, 126.4, 126.7, 129.5, 130.0, 131.6, 131.8, 132.0, 135.4, 140.9, 148.1, 152.4, 163.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 460.6 (21000), 491.4 (51100), 528.8 nm (70800). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 536.3 (1.00), 578.8 (0.51), 628.0 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0203, reference **S-13** with Φ = 1.00): 1.00. MS (FAB^+): *m/z* (%):

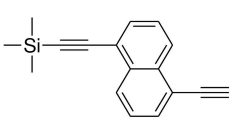
846.1 (100) [M^++H], 664.0 (68), 391.1 (32), 373.1 (72), 345.1 (48). HRMS ($C_{55}H_{52}N_3O_4Si$): Calcd. 846.3727 [M^++H], found 846.3734 [M^++H]; Δ = +0.0007. $C_{55}H_{51}N_3O_4Si$ (846.0): Calcd. C 78.07, H 6.08, N 4.97; found C 78.20, H 6.01, N 4.88.



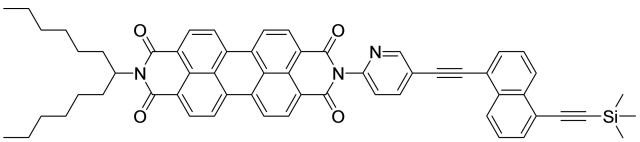
2-[5-(4-Ethynylphenylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone: 2-(1-Hexylheptyl)-9-[5-(4-trimethylsilanylethynylphenylethynyl)pyridin-2-yl]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**2**, 65 mg, 77 µmol) was dissolved in THF (5.3 mL), stirred with tetrabutylammoniumfluoride (TBAF, 0.17 mmol, 0.17 mL, 1 M in THF), diluted with distilled water, extracted with chloroform (3×), dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel, chloroform/ethanol 80 : 1). Yield 35 mg (59 %) red solid, m.p. > 250 °C. R_f -value (chloroform/ethanol 80 : 1) = 0.25. IR (ATR): $\tilde{\nu}$ = 3292.4 (w), 2922.6 (w), 2853.1 (w), 2361.1 (w), 2338.0 (w), 1695.6 (m), 1653.1 (s), 1592.1 (s), 1576.3 (m), 1505.9 (w), 1465.0 (w), 1431.7 (w), 1403.6 (m), 1339.1 (s), 1249.2 (m), 1174.0 (w), 1123.6 (w), 1103.2 (w), 1024.5 (w), 964.0 (w), 835.9 (m), 809.1 (s), 742.4 (m), 667.5 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, ^3J(H,H) = 7.1 Hz, 6 H, 2×CH_3), 1.18–1.38 (m, 16 H, 8×CH_2), 1.83–1.91 (m, 2 H, β-CH_2), 2.21–2.29 (m, 2 H, β-CH_2), 3.21 (s, 1 H, CH_{Alkin}), 5.16–5.22 (m, 1 H, N–CH), 7.46 (d, ^3J(H,H) 8.2 Hz, 1 H, $CH_{pyridine}$), 7.50–7.56 (m, 4 H, 4×$CH_{aromat.}$), 8.06 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.63–8.74 (m, 8 H, 8×$CH_{perylene}$), 8.87 ppm (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 26.9, 29.2, 31.7, 32.4, 54.8, 79.4, 83.1, 87.1, 93.1, 120.9, 122.7, 123.0, 123.1, 123.4, 123.8, 126.4, 126.7, 129.5, 130.0, 131.7, 131.8, 132.2, 135.4, 140.9, 148.2, 152.4, 163.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 460.6 (0.25), 491.4 (0.62), 528.0 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.4 (1.00), 578.4 (0.51), 627.4 nm (0.12). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0140, reference **S-13** with Φ = 1.00): 1.00. MS (FAB$^+$): *m/z* (%): 774.4 (57) [M^++H], 592.2 (54), 391.2 (30), 373.1 (100), 345.2 (55), 275.2 (20). HRMS ($C_{52}H_{43}N_3O_4$): Calcd. 774.3332 [M^++H], found 774.3339 [M^++H]; Δ = +0.0007.



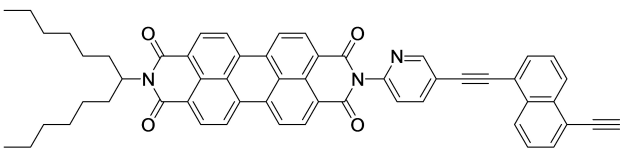
2,10-Bis(1-hexylheptyl)-6-{4'-[3,8,9,10-tetrahydro-9-(1-hexyl-heptyl)-1,3,8,10-tetraoxo]anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-2(1*H*)-yl}-[5-(5-pyridin-2-yl-1-ethynyl-phen-4-ylethynyl)pyridin-2-yl]-1*H*-pyrrolo[3',4':4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (4): 2-[5-(4-Ethynylphenylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (27 mg, 35 µmol) under argon atmosphere, *N,N''*-bis(1-hexylheptyl)-*N'*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1',2':3,4 : 9,10-hexacarboxylic-1',2':3,4 : 9,10-tris(dicarboximide) (**3**, 33 mg, 31 µmol)), $PdCl_2(PPh_3)_2$ (2.5 mg, 3.5 µmol), CuI (1.0 mg, 2.5 µmol) and PPh_3 (1.0 mg, 3.5 µmol), dissolved in THF (3.0 mL) and triethylamine (1.5 mL) were stirred at 80 °C (bath) for 16 h, evaporated in vacuo stirred in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (fine silica gel, 300×44 mm), chloroform/ethanol 70 : 1). Yield 27 mg (51 %) orange solid, m.p. > 250 °C. R_f -value (chloroform/ethanol 60 : 1) = 0.45. IR (ATR): $\tilde{\nu}$ = 2923.0 (w), 2854.3 (w), 2360.3 (m), 2338.9 (m), 1700.0 (s), 1660.3 (s), 1593.1 (m), 1506.7 (w), 1465.9 (w), 1404.0 (w), 1364 (s), 1339.4 (s), 1317.2 (s), 1246.9 (w), 1169.0 (w), 946.1 (w), 835.5 (w), 809.9 (s), 764.5 (w), 746.5 (m), 667.7 (m), 659.6 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.79–0.89 (m, 18 H, 6×CH_3), 1.18–1.51 (m, 48 H, 24×CH_2), 1.88–1.96 (m, 2 H, β-CH_2), 1.96–2.04 (m, 4 H, 2×β-CH_2), 2.23–2.32 (m, 2 H, β-CH_2), 2.32–2.40 (4 H, 2×β-CH_2), 5.16–5.23 (m, 1 H, N–CH), 5.27–5.38 (m, 2 H, 2×N–CH), 7.42 (d, ^3J(H,H) = 8.0 Hz, 1 H, $CH_{pyridine}$), 7.54–7.64 (m, 4 H, 4×$CH_{aromat.}$), 7.80 (d, ^3J(H,H) = 7.8 Hz, 1 H, $CH_{pyridine}$), 8.05 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.13 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.29–8.66 ppm (m, 8 H, 8×$CH_{perylene}$), 8.87 (s, 1 H, $CH_{pyridine}$), 8.94 (s, 1 H, $CH_{pyridine}$), 9.06–9.27 (m, 4 H, 4×$CH_{perylene}$), 10.37 ppm (s, 2 H, 2×$CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0 27.1, 29.3, 29.4, 29.7, 31.8, 31.9, 32.4, 54.9, 55.3, 87.5, 93.0, 93.3, 120.2, 120.7, 121.6, 122.7, 122.8, 123.0, 123.1, 123.9, 124.8, 125.8, 126.3, 126.8, 127.5, 127.9, 129.1, 129.7, 131.6, 131.8, 134.8, 140.9, 151.8, 163.0, 166.1 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 436.6 (0.50), 466.4 (0.82), 491.2 (0.63), 528.0 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 436 nm): λ_{max} (I_{rel}) = 535.8 (1.00), 578.5 nm (0.50). ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.6 (1.00), 578.4 nm (0.50). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm/1\ cm}$ = 0.0126, reference **C-25** with Φ = 1.00): 0.93. ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0159, reference **C-25** with Φ = 1.00): 1.00. MS (FAB$^+$): *m/z* (%): 1696.9 (0.3) [M^++H], 1514.7 (0.1), 1332.5 (0.1), 1150.4 (0.1). HRMS ($C_{111}H_{106}N_7O_{10}$): Calcd. 1696.8001 [M^++H], found 1696.8031 [M^++H]; Δ = +0.0030.



(5-Ethynylnaphthalen-1-ylethynyl)trimethylsilane: 1,5-Diethynylnaphthalene (204 mg, 1.16 mmol) under argon atmosphere was dissolved in THF (2.5 mL), cooled to - 60 °C, treated dropwise with ethylmagnesiumbromide (1 M in THF, 1.16 mL, 1.16 mmol), allowed to warm at 0 °C, treated with chlorotrimethylsilane (125 mg, 1.16 mmol), stirred at 80 °C (bath) for 3 h, treated with saturated aqueous NH_4Cl solution, separated with the organic phase, washed with distilled water and then with saturated brine, dried with $MgSO_4$. and evaporated in vacuo. Yield 139 mg (48 %) colorless powder. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 0.32$ (s, 9 H, $Si(CH_3)_3$), 3.47 (s, 1 H, CH_{alkyne}), 7.47–7.53 (m, 2 H, 2× $CH_{aromat.}$), 7.71–7.78 (m, 2 H, 2× $CH_{aromat.}$), 8.30–8.39 ppm (m, 2 H, 2× $CH_{aromat.}$). MS (DEP/EI): *m/z* (%): 248.2 (100) [M^+], 233.2 (42) [M^+-CH_3], 189.2 (18), 116.6 (12). HRMS ($C_{17}H_{16}{}^{28}Si$): Calcd. 248.1021 [M^+], found 248.1002 [M^+]; Δ =- 0.0019.

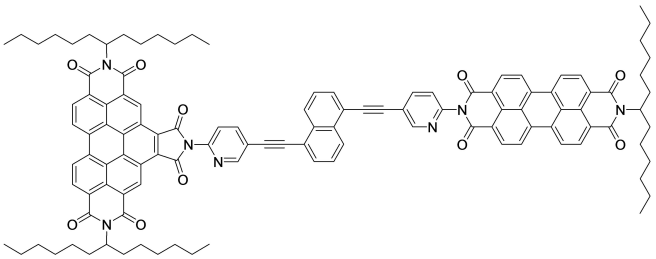


2-(1-Hexylheptyl)-9-[5-(5-trimethylsilanylethynylnaphthalen-1-ylethynyl)pyridin-2-yl]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone: 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (250 mg, 323 µmol) under argon atmosphere, (5-ethynylnaphthalen-1-ylethynyl) trimethylsilane (139 mg, 561 µmol), $PdCl_2(PPh_3)_2$ (23 mg, 32 µmol), CuI (6.1 mg, 32 µmol) and PPh_3 (8.4 mg, 32 µmol), dissolved in THF (6.5 mL) and triethylamine (3.3 mL) were stirred at 80 °C (bath) for 6 h, evaporated in vacuo stirred in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel, 800 × 44 mm), chloroform/ethanol 100 : 1). Yield 144 mg (50 %) bright red solid, m.p. > 250 °C. R_f -value (chloroform/ethanol 100 : 1) = 0.40. IR (ATR): $\tilde{\nu} = 2952.1$ (w), 2924.1 (m), 2854.3 (w), 1698.2 (m), 1670.1 (s), 1658.5 (s), 1594.1 (m), 1577.5 (w), 1503.8 (w), 1480.7 (w), 1466.2 (w), 1431.8 (w), 1404.7 (w), 1351.3 (m), 1341.9 (s), 1250.1 (s), 1199.1 (w), 1176.7 (m), 1120.9 (w), 1107.1 (w), 1025.1 (w), 964.2 (w), 926.9 (w), 916.6 (w), 858.8 (m), 844.8 (s), 812.1 (w), 793.2 (s), 760.9 (w), 745.6 cm^{-1} (s). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 0.34$ (s, 9 H, $Si(CH_3)_3$), 0.82 (t, ^3J(H,H) = 7.0 Hz, 6 H, 2× CH_3), 1.18–1.38 (m, 16 H, 8× CH_2), 1.83–1.91 (m, 2 H, β-CH_2), 2.20–2.28 (m, 2 H, β-CH_2), 5.15–5.21 (m, 1 H, N–CH), 7.50 (d, ^3J(H,H) = 8.1 Hz, 1 H, $CH_{pyridine}$), 7.53–7.59 (m, 2 H, 2× $CH_{aromat.}$), 7.76 (d, ^3J(H,H) = 6.9 Hz, 1 H, $CH_{aromat.}$), 7.84 (d, ^3J(H,H) = 7.0 Hz, 1 H, $CH_{aromat.}$), 8.16 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.1 Hz, 1 H, $CH_{pyridine}$), 8.40 (d, ^3J(H,H) = 8.4 Hz, 2 H, 2× $CH_{aromat.}$), 8.57–8.72 (m, 8 H, 8× $CH_{perylene}$), 8.97 ppm (d, ^4J(H,H) = 2.0 Hz, 1 H, $CH_{pyridine}$). ^{13}C-NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 0.1$, 14.0, 22.6, 26.9, 29.2, 31.7, 32.6, 54.8, 90.4, 91.7, 100.2, 102.6, 120.3, 121.2, 121.4, 123.0, 123.4, 123.9, 126.3, 126.7, 125.9, 127.9, 129.5, 130.0, 131.1, 131.5, 131.8, 132.9, 133.2, 134.2, 135.3, 141.0, 148.1, 152.4, 163.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 459.8 (23100), 491.2 (59100), 528.0 nm (96400). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.5 (1.00), 577.9 (0.50), 629.4 nm (0.12). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0133, reference **S-13** with $\Phi = 1.00$): 1.00. MS (DEP/EI): *m/z* (%): 895.4 (38) [M^+], 713.2 (100), 349.6 (69). HRMS ($C_{59}H_{53}N_3O_4Si$): Calcd. 865.3805 [M^+], found 895.3788 [M^+]; Δ =- 0.0017. $C_{59}H_{53}N_3O_4Si$ (896.2): Calcd. C 79.07, H 5.96, N 4.69; found C 78.67, H 5.94, N 4.53.

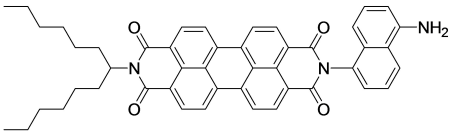


2-[5-(5-Ethynylnaphthalen-1-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone: 2-(1-Hexylheptyl)-9-[5-(5-trimethylsilanylethynylnaphthalen-1-ylethynyl)pyridin-2-yl]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (120 mg, 134 µmol) was dissolved in THF (10 mL), stirred with tetrabutylammoniumfluoride (TBAF, 0.26 mmol, 0.26 mL, 1 M in THF), diluted with distilled water, extracted with chloroform (3×), dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel, chloroform/ethanol 100 : 1). Yield 101 mg (98 %) bright red solid, m.p. > 250 °C. R_f -value (chloroform/ethanol 100 : 1) = 0.45. IR (ATR): $\tilde{\nu} = 3303.8$ (w), 2951.9 (w), 2921.9 (m), 2853.3 (w), 2358.1 (w), 1702.1 (w), 1692.4 (s), 1651.1 (s), 1593.6 (s), 1578.8 (m), 1508.0 (w), 1481.2 (w), 1466.1 (w), 1455.0 (w), 1434.6 (w), 1406.3 (m), 1374.4 (w), 1342.8 (s), 1307.3 (w), 1248.9 (s), 1202.3 (w), 1192.4 (w), 1174.0 (m), 1163.1 (w), 1142.2 (w), 1126.0 (w), 1105.3 (w), 1030.9 (w), 965.1 (w), 849.7 (m), 839.8 (w), 809.9 (m), 793.0 (s), 743.9 cm^{-1} (s). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 0.82$ (t, ^3J(H,H) = 7.0 Hz, 6 H, 2× CH_3), 1.17–1.38 (m, 16 H, 8× CH_2), 1.83–1.90 (m, 2 H, β-CH_2), 2.20–2.28 (m, 2 H, β-CH_2), 3.50 (s, 1 H, CH_{alkyne}), 5.15–5.21 (m, 1 H, N–CH), 7.50 (d, ^3J(H,H) = 8.1 Hz, 1 H, $CH_{pyridine}$), 7.56–7.70 (m, 2 H, 2× $CH_{aromat.}$), 7.80 (d, ^3J(H,H) = 6.9 Hz, 1 H, $CH_{aromat.}$), 7.86 (d, ^3J(H,H) = 7.0 Hz, 1 H, $CH_{aromat.}$), 8.17 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.1 Hz, 1 H, $CH_{pyridine}$), 8.41–8.45 (m, 2 H, 2× $CH_{aromat.}$), 8.61–8.74 (m, 8 H, 8× $CH_{perylene}$), 8.98 ppm (d, ^4J(H,H) = 2.1 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 14.0$, 22.5, 26.9, 29.2, 29.7, 31.7, 32.4, 54.8, 81.4, 82.6, 90.4, 91.6, 120.4, 121.2, 123.0, 123.1, 123.4, 123.9, 126.3, 126.4, 126.7, 127.3, 127.7, 129.5, 130.0, 131.5, 131.9, 132.9, 133.3, 134.2, 135.4, 141.0, 148.2, 152.4, 163.4 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 460.2 (24000), 491.4 (59900), 528.2 nm (97100). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 536.4 (1.00), 579.3 (0.50), 627.2 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0140, reference **S-13** with $\Phi = 1.00$): 1.00. MS (FAB$^+$): *m/z* (%): 824.5 (45) [M^+ + H], 642.3 (24), 391.2 (12), 373.2 (40), 251.1 (10). HRMS ($C_{56}H_{45}N_3O_4$):

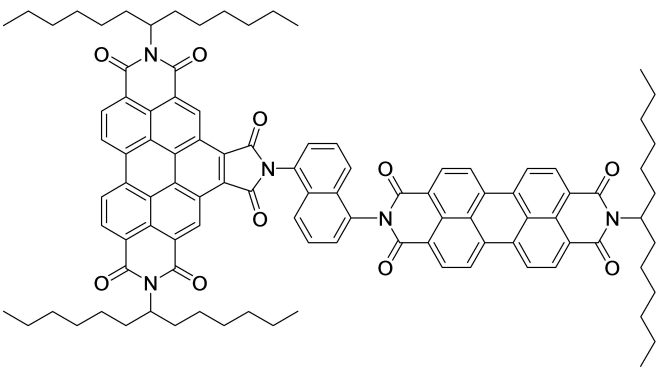
Calcd. 824.3488 [M^+], found 824.3472 [M^+]; Δ =- 0.0016. $C_{56}H_{45}N_3O_4$ (823.3): Calcd. C 81.63, H 5.50, N 5.10; found C 81.58, H 5.58, N 4.97.



2,10-Bis(1-hexylheptyl)-6-{4'-[3,8,9,10-tetrahydro-9-(1-hexylheptyl)-1,3,8,10-tetraoxo]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-2(1*H*)-yl}-[5-(5-pyridin-2-yl-1-ethynyl-naphthalen-5-ylethynyl)pyridin-2-yl]-1*H*-pyrrolo[3',4':4,5]pyreno[2,1,10-*def*:7,8,9-*d'e'f'*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexaone (5): 2-[5-(5-Ethynylnaphthalen-1-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (83 mg, 0.10 mmol) under argon atmosphere, *N,N'*-bis(1-hexylheptyl)-*N'*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1',2':3,4:9,10-hexacarboxylic-1',2':3,4:9,10-tris (dicarboximide) (**3**, 118 mg, 112 µmol), $PdCl_2(PPh_3)_2$ (7.2 mg, 10 µmol), CuI (2.6 mg, 10 µmol) and PPh_3 (2.6 mg, 10 µmol), dissolved in THF (10 mL) and triethylamine (5.0 mL) were stirred at 80 °C (bath) for 16 h, evaporated in vacuo stirred in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (fine silica gel, 600 × 44 mm), chloroform/ethanol 50:1). Yield 90 mg (51 %) orange solid, m.p. > 250 °C. R_f -value (chloroform/ethanol 50:1) = 0.55. IR (ATR): $\tilde{\nu}$ = 2924.6 (m), 2855.3 (w), 2361.6 (w), 2337.3 (w), 2155.5 (w), 1773.0 (w), 1700.8 (m), 1660.0 (s), 1626.3 (w), 1594.0 (m), 1578.0 (m), 1521.6 (w), 1505.7 (w), 1478.4 (w), 1431.0 (w), 1404.2 (w), 1364.4 (m), 1340.0 (s), 1318.1 (m), 1278.0 (w), 1248.6 (m), 1200.6 (w), 1169.4 (w), 1124.6 (w), 1105.7 (w), 1024.2 (w), 965.6 (m), 941.7 (w), 887.8 (w), 849.9 (m), 810.5 (s), 790.3 (m), 765.8 (w), 747.5 (m), 725.9 (w), 701.7 (w), 659.6 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.82–0.87 (m, 18 H, 6 × CH_3), 1.23–1.47 (m, 48 H, 24 × CH_2), 1.89–1.97 (m, 2 H, β-CH_2), 1.98–2.09 (m, 4 H, 2 × β-CH_2), 2.23–2.32 (m, 2 H β-CH_2), 2.34–2.46 (m, 4 H, 2 × β-CH_2), 5.17–5.23 (m, 1 H, N–CH), 5.29–5.40 (m, 2 H, 2 × N–CH), 7.00 (s, 1 H, $CH_{aromat.}$), 7.38 (s, 1 H, $CH_{aromat.}$), 7.53–7.65 (m, 3 H, 2 × $CH_{aromat.}$, $CH_{pyridine}$), 7.80–7.90 (m, 2 H, 2 × $CH_{aromat.}$), 8.14 (s, 1 H, $CH_{pyridine}$), 8.22 (s, 1 H, $CH_{pyridine}$), 8.30–8.70 (m, 10 H, 8 × $CH_{perylene}$, 2 × $CH_{pyridine}$), 8.91 (s, 1 H, $CH_{pyridine}$), 9.03–9.14 (m, 4 H, 4 × $CH_{perylene}$), 10.23 ppm (s, 2 H, 2 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.1, 22.6, 27.1, 27.2, 29.3, 31.8, 31.9, 32.4, 54.9, 55.3, 90.4, 91.6, 122.5, 122.8, 124.3, 125.6, 126.3, 127.2, 130.8, 131.5, 132.9, 140.6, 144.8, 148.3, 151.6, 151.8, 163.1, 165.8 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 408.6 (21900), 437.2 (44200), 466.8 (74100), 491.2 (56900), 528.2 nm (91800). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 536.3 (1.00), 579.3 nm (0.50). ($CHCl_3$, λ_{exc} = 437 nm): λ_{max} (I_{rel}) = 536.0 (1.00), 579.3 nm (0.49). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0092, reference **C-25** with Φ = 1.00): 1.00. ($CHCl_3$, λ_{exc} = 437 nm, $E_{437\ nm/1\ cm}$ = 0.0070, reference C-25 with Φ = 1.00): 0.92. MS (FAB^+): *m/z* (%): 1747.7 (1) [M^+ + H], 1564.7 (1), 1382.5 (1), 1200.3 (1). HRMS ($C_{115}H_{108}N_7O_{10}$): Calcd. 1746.8158 [M^+ + H], found 1746.8131 [M^+ + H]; Δ = -0.0027. $C_{115}H_{107}N_7O_{10}$ (1745.8): Calcd. C 79.06, H 6.17, N 5.61; found C 78.82, H 6.12, N 5.55.

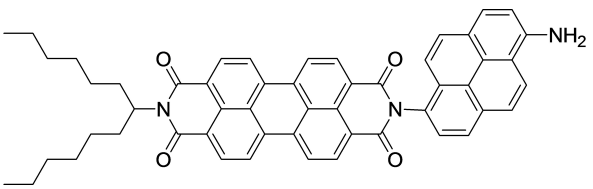


2-(5-Aminonaphthalen-1-yl)-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (7): 9-(1-Hexylheptyl)-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (**6**) (218 mg, 380 µmol), 1,5-diaminonaphthalene (63 mg, 0.40 mmol) and imidazole (12 g) were stirred at 150 °C for 3 h, still warm treated with ethanol (20 mL) and then with 2 M aqueous HCl (100 mL), collected by vacuum filtration, dried at 110 °C and used for the subsequent reaction without further purification. Yield 220 mg (77 %) dark violet dye. MS (FAB^+): *m/z* (%): 714.9 (90) [M^+ + H], 713.8 (52) [M^+], 653.8 (11), 573.7 (9), 532.6 (54), 531.6 (27), 486.5 (10).

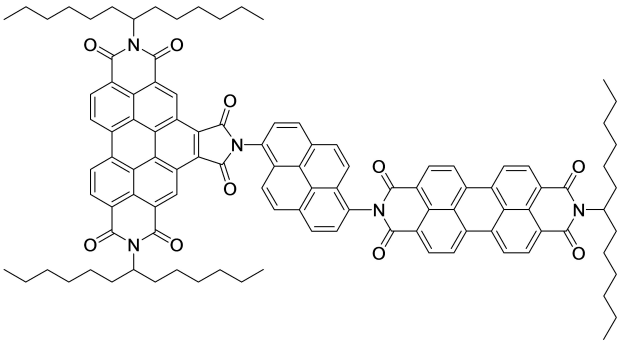


***N*²,*N*³-Bis(1-hexylheptyl)-*N*¹-[*N*-(1-hexylheptyl)-*N'*-(1,5-naphthalen)perylene-2,3:8,9-tetracarboxbisimide]benzo[*ghi*]perylene-2,3:8,9:11,12-hexacarboxtrisimide (9)**: *N,N'*-Bis(1-hexylheptyl)benzo[*ghi*]perylene-2,3,8,9,11,12-hexacarboxylic-2,3:8,9-bis(dicarboximide)-11,12-anhydride (**8**) (261 mg, 308 µmol), 2-(5-aminonaphthalen-1-yl)-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (7, (220 mg, 308 µmol) and quinoline (30 mL) were stirred at 150 °C for 20 h, still warm treated with 2 M aqueous HCl (150 mL), collected by vacuum filtration, dried at 110 °C and purified by column separation (silica gel 800 × 44 mm); chloroform/ethanol 80:1). Yield 99 mg (21 %) orange red dye, m.p. > 250 °C. R_f -value ($CHCl_3$/EtOH 80:1) = 0.40. IR (ATR): $\tilde{\nu}$ = 3075.3 (w), 2952.3 (w), 2923.9 (m), 2854.6 (m), 2362.6 (w), 2339.0 (w), 1775.9 (w),

1714.5 (s), 1702.1 (s), 1659.6 (s), 1627.3 (w), 1593.6 (s), 1579.7 (m), 1522.2 (w), 1508.3 (w), 1456.8 (w), 1404.0 (m), 1363.1 (s), 1337.7 (s), 1317.0 (s), 1275.7 (m), 1244.1 (m), 1218.9 (m), 1202.2 (m), 1174.2 (m), 1135.6 (w), 1125.7 (m), 1108.2 (m), 1078.1 (w), 971.0 (m), 943.3 (w), 901.7 (w), 851.6 (m), 810.1 (s), 796.6 (m), 782.8 (m), 765.8 (m), 745.9 (s), 727.3 (m), 659.8 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 0.76–0.91$ (m, 18 H, $6 \times CH_3$), 1.13–1.50 (m, 48 H, $24 \times CH_2$), 1.84–1.92 (m, 2 H, β-CH_2), 1.93–2.03 (m, 4 H, $2 \times \beta$-CH_2), 2.22–2.30 (m, 2 H, β-CH_2), 2.31–2.40 (m, 4 H, $2 \times \beta$-CH_2), 5.17–5.25 (m, 1 H, N–CH), 5.27–5.37 (m, 2 H, $2 \times$ N–CH), 7.57–7.77 (m, 4 H, $4 \times CH_{aromat.}$), 7.88–7.93 (m, 1 H, $CH_{aromat.}$), 7.95–8.04 (m, 1 H, $CH_{aromat.}$), 8.53–8.85 (m, 8 H, $8 \times CH_{perylene}$), 9.12–9.48 (m, 4 H, $4 \times CH_{perylene}$), 10.52 ppm (s, 2 H, $2 \times CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 14.0$, 22.6, 27.0, 29.2, 31.8, 32.4, 54.8, 55.3, 123.1, 123.2, 123.3, 123.5, 124.2, 125.2, 127.5, 127.8, 132.1, 135.3, 163.6 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 435.6 (59400), 466.0 (88800), 491.0 (69800), 527.8 nm (104400). Fluorescence ($CHCl_3$, $\lambda_{exc} = 491$ nm): λ_{max} (I_{rel}) = 536.4 (1.00), 578.7 (0.50), 626.7 nm (0.11). ($CHCl_3$, $\lambda_{exc} = 436$ nm): λ_{max} (I_{rel}) = 535.7 (1.00), 577.9 (0.49), 626.9 nm (0.11). Fluorescence quantum yield ($CHCl_3$, $\lambda_{exc} = 491$ nm, $E_{491nm/1\ cm} = 0.0113$, reference: **C-25** with $\Phi = 1.00$): 1.00. ($CHCl_3$, $\lambda_{exc} = 436$ nm, $E_{436nm/1\ cm} = 0.0086$, reference: C-25 with $\Phi = 1.00$): 0.98. MS (FAB$^+$): *m/z* (%): 1545.0 (1) [$M^+ + H$], 1362.7 (1), 1180.3 (1), 998.0 (2), 558.0 (1), 499.6 (1), 391.0 (3), 373.4 (8). HRMS ($C_{101}H_{101}N_5O_{10}$): Calcd. 1545.7660 [$M^+ + H$], found 1545.7631 [$M^+ + H$]; $\Delta = -0.0029$. $C_{101}H_{101}N_5O_{10}$ (1543.8): Calcd. C 78.52, H 6.59, N 4.53; found C 77.71, H 6.65, N 4.44.



2-(6-Aminopyren-1-yl)-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (11): 9-(1-Hexylheptyl)-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (**6**, 218 mg, 380 µmol), 1,6-diaminopyrene (**10**, 117 mg, 400 µmol) and imidazole (12 g) were stirred at 150 °C for 3 h, still warm treated with ethanol (20 mL) and then shaken with 2 M aqueous HCl (100 mL), collected by vacuum filtration, dried at 110 °C and used for the subsequent reaction without further purification. Yield 226 mg, red solid. MS (FAB$^+$): *m/z* (%): 788.8 (13) [$M^+ + H$], 787.8 (13) [M^+], 606.6 (7), 573.6 (9), 391.4 (23), 345.0 (14), 273.0 (23), 217.0 (11).



***N*²,*N*³-Bis(1-hexylheptyl)-*N*¹-[*N*-(1-hexylheptyl)-*N′*-(1,6-pyrene)perylene-2,3 : 8,9-tetracarboxbisimide]benzo[*ghi*]perylene-2,3 : 8,9 : 11,12-hexacarboxtrisimide (12)**: *N*,*N′*-Bis(1-hexylheptyl)benzo[*ghi*]perylene-2,3,8,9,11,12-hexacarboxylic-2,3 : 8,9-bis(dicarboximide)-11,12-anhydride (**11**, 261 mg, 308 µmol), 2-(6-aminopyren-1-yl)-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (**8**, 650 mg, 2.95 mmol) and quinoline (30 mL) were stirred at 150 °C for 18 h, still warm treated with 2 M aqueous HCl (150 mL), collected by vacuum filtration, dried at 110 °C and purified by column separation (fine silica gel 300 × 44 mm, chloroform). Yield 36 mg (7 %) dark red solid, m.p. > 250 °C. R_f -value ($CHCl_3$) = 0.50. IR (ATR): $\tilde{\nu} = 3071.4$ (w), 2652.3 (w), 2923.7 (m), 2854.4 (m), 2361.1 (w), 1776.9 (w), 1704.5 (s), 1659.1 (s), 1625.3 (m), 1592.9 (s), 1551.7 (w), 1529.6 (w), 1501.1 (w), 1480.4 (w), 1462.0 (w), 1443.9 (m), 1431.0 (w), 1403.8 (m), 1363.4 (s), 1337.8 (s), 1316.1 (s), 1274.4 (m), 1245.5 (m), 1200.9 (m), 1173.4 (m), 1135.6 (m), 1104.8 (m), 1018.7 (w), 963.0 (w), 943.3 (w), 866.0 (w), 842.7 (m), 809.5 (s), 780.9 (m), 764.7 (m), 744.1 (s), 719.3 (m), 697.9 (w), 680.0 (w), 659.4 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 0.74–0.95$ (m, 18 H, $6 \times CH_3$), 1.11–1.36 (m, 48 H, $24 \times CH_2$), 1.84–2.10 (m, 8 H, $4 \times \beta$-CH_2), 2.21–2.46 (m, 4 H, $2 \times \beta$-CH_2), 5.16–5.25 (m, 1 H, N–CH), 5.32 (bs, 2 H, $2 \times$ N–CH), 7.89–7.96 (m, 2 H, $2 \times CH_{aromat.}$), 8.01–8.20 (m, 4 H, $4 \times CH_{aromat.}$), 8.30–8.38 (m, 2 H, $2 \times CH_{aromat.}$), 8.40–8.72 (m, 8 H, $8 \times CH_{perylene}$), 9.08–9.30 (m, 4 H, $4 \times CH_{perylene}$), 10.51 ppm (s, 2 H, $2 \times CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta = 14.0$, 22.6, 27.0, 29.2, 29.7, 31.8, 32.5, 54.9, 55.3, 122.6, 123.0, 123.1, 123.3, 123.4, 124.1, 125.2, 125.3, 125.9, 126.1, 127.2, 127.5, 128.3, 128.4, 130.1, 131.7, 132.1, 133.3, 135.1, 163.8, 167.8 ppm. UV/VIS ($CHCl_3$): λ_{max} (E_{rel}) = 376.8 (0.63), 436.0 (0.47), 491.6 (0.63), 528.8 nm (1.00). MS (FAB$^+$): *m/z* (%): 1619.3 (0.5) [$M^+ + H$], 1618.3 (0.4), [M^+], 1436.3 (0.3), 1255.4 (0.2), 1073.1 (0.2), 766.9 (0.3), 391.0 (1), 373.5 (2). HRMS ($C_{107}H_{103}N_5O_{10}$): Calcd. 1618.7738 [M^+], found 1618.7750 [M^+]; $\Delta = +0.0012$.

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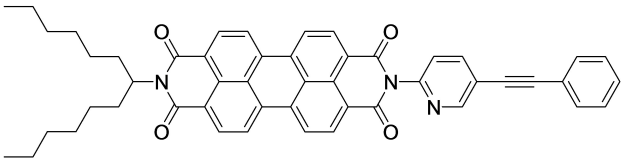
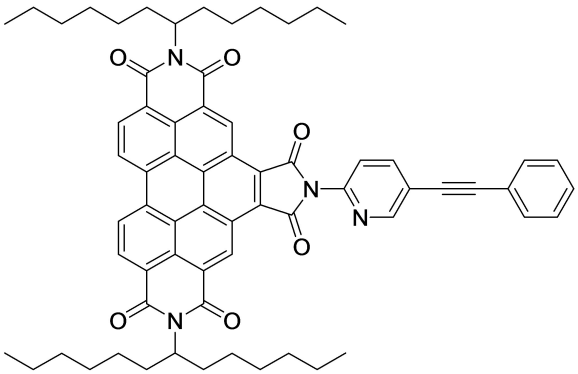
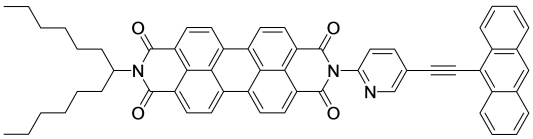


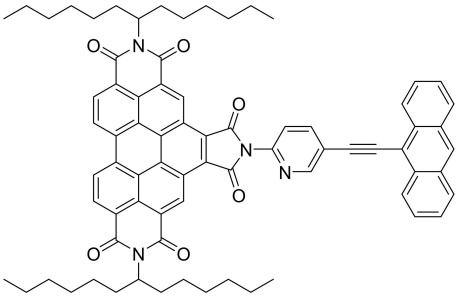
2-[5-(Phenylethynyl)pyridin-2-yl]-9-(1-hexylheptyl) anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (14): 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**1**, 100 mg, 129 μmol) under argon atmosphere was dissolved in THF (5.0 mL), treated with $PdCl_2(PPh_3)_2$ (15 mg, 13 μmol), CuI (3.2 mg, 17 μmol), PPh_3 (3.4 mg, 13 μmol), then treated with phenylethyne (66 mg, 0.65 mmol), triethylamine (2.5 mL), stirred at 80 °C (bath) for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 800 × 44 mm, chloroform/ethanol 80 : 1). Yield 80 mg (83 %) red dye, m.p. > 250 °C. R_f -value ($CHCl_3$/EtOH 80 : 1) = 0.30. IR (ATR): $\tilde{\nu}$ = 3054.9 (w), 2953.8 (w), 2924.8 (w), 2855.1 (w), 2361.5 (w), 2336.2 (w), 2224.1 (w), 1707.0 (m), 1695.1 (m), 1655.0 (s), 1615.4 (w), 1593.1 (m), 1577.3 (m), 1506.0 (w), 1493.7 (w), 1466.9 (w), 1456.8 (w), 1441.7 (w), 1432.6 (w), 1403.8 (m), 1353.3 (m), 1341.0 (s), 1320.0 (w), 1251.0 (m), 1196.6 (w), 1175.3(m), 1138.5 (w), 1125.3 (w), 1107.1 (w), 1069.2 (w), 1025.9 (w), 998.8 (w), 965.2 (w), 925.5 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, $^3J(H,H)$ = 7.0 Hz, 6 H, 2 × CH_3), 1.18–1.42 (m, 16 H, 8 × CH_2), 1.83–1.98 (m, 2 H, β-CH_2), 2.21–2.28 (m, 2 H, β-CH_2), 5.15–5.22 (m, 1 H, N–CH), 7.37–7.42 (m, 3 H, 3 × $CH_{aromat.}$), 7.45 (d, $^3J(H,H)$ = 8.1 Hz, 1 H, $CH_{pyridine}$), 7.55–7.62 (m, 2 H, 2 × $CH_{aromat.}$), 8.06 (dd, $^3J(H,H)$ = 8.0 Hz, $^4J(H,H)$ = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.62- 8.69 (m, 8 H, 8 × $CH_{perylene}$), 8.88 ppm (d, $^4J(H,H)$ = 2.3 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 1.0, 14.0, 22.6, 26.9, 29.2, 31.7, 32.4, 54.8, 85.3, 93.8, 121.3, 122.3, 123.0, 123.4, 123.7, 126.4, 126.7, 128.5, 129.0, 129.5, 130.0, 131.8, 134.2, 135.4, 140.9, 147.9, 152.3, 163.3 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 459.6 (25000), 491.2 (59000), 527.8 nm (94400). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.5 (1.00), 578.2 (0.50), 627.4 nm (0.12). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491nm/1\ cm}$ = 0.0141, reference: **S-13** with Φ = 1.00): 1.00. MS (FAB^+): *m/z* (%): 750.6 (34) [$M+H^+$], 568.4 (52), 373.3 (100), 345.3 (50). HRMS ($C_{50}H_{43}N_3O_4$): Calcd. 750.3326 [M^+], found 750.3332 [M^+]; Δ = +0.0006. $C_{50}H_{43}N_3O_4$ (749.33): Calcd. C 80.08, H 5.78, N 5.60; found C 79.90, H 5.82 N 5.59.



***N,N″*-Bis-(1-hexylheptyl)-*N′*-[5-(phenylethynyl)pyridin-2-yl]benzo[*ghi*]perylene-1′,2′:3,4 : 9,10-hexacarboxylic-1′,2′:3,4 : 9,10-tris(dicarboximide) (13)**: *N,N′*-Bis(1-hexylheptyl)-*N′*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1′,2′:3,4 : 9,10-hexacarboxylic-1′,2′:3,4 : 9,10-tris(dicarboximide) (**3**, 100 mg, 95.2 μmol) under argon atmosphere was dissolved in THF (4.0 mL), treated with $PdCl_2(PPh_3)_2$ (11 mg, 10 μmol), CuI (2.2 mg, 13 μmol), PPh_3 (3.0 mg, 10 μmol), then treated with phenylethyne (39 mg, 0.38 mmol), triethylamine (2.0 mL), stirred at 80 °C (bath) for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 800 × 44 mm, chloroform). Yield 63 mg (65 %) yellow dye, m.p. > 250 °C. R_f -value ($CHCl_3$) = 0.80. IR (ATR): $\tilde{\nu}$ = 3076.4 (w), 2953.7 (m), 2924.0 (m), 2855.3 (m), 2219.7 (w), 1717.8 (s), 1706.2 (s), 1662.8 (s), 1625.7 (m), 1594.8 (m), 1561.9 (m), 1523.0 (w), 1494.1 (m), 1467.9 (m), 1413.7 (m), 1364.4 (s), 1316.8 (s), 1277.2 (m), 1262.1 (m), 1242.4 (m), 1203.5 (m), 1168.1 (m), 1122.6 (m), 1099.8 (m), 1070.0 (m), 1023.9 (m), 964.5 (m), 942.5 (m), 886.3 (w), 846.4 (m), 810.2 (s), 763.8 (s), 747.2 (s), 724.6 (m), 690.5 (m), 695.6 cm^{-1} (m). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, $^3J(H,H)$ = 6.9 Hz, 12 H, 4 × CH_3), 1.15–1.47 (m, 32 H, 16 × CH_2), 1.94–2.02 (m, 4 H, 2 × β-CH_2), 2.27–2.41 (m, 4 H, 2 × β-CH_2), 5.25–5.37 (m, 2 H, 2 × N–CH), 7.38–7.46 (m, 3 H, 3 × $CH_{aromat.}$), 7.58–7.66 (m, 2 H, 2 × $CH_{aromat.}$), 7.79 (d, $^3J(H,H)$ = 8.1 Hz, 1 H, $CH_{pyridine}$), 8.16 (dd, $^3J(H,H)$ = 8.2 Hz, $^4J(H,H)$ = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.92 (dd, $^4J(H,H)$ = 2.3 Hz, 1 H, $CH_{pyridine}$), 9.19–9.44 (m, 4 H, 4 × $CH_{perylene}$), 10.46 ppm (s, 2 H, 2 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 29.2, 29.7, 31.8, 32.4, 55.3, 93.9, 103.9, 121.5, 123.4, 124.1, 125.0, 127.0, 127.8, 128.2, 128.5, 129.1, 131.8, 133.3, 140.8, 152.0, 166.3 ppm. UV/VIS ($CHCl_3$): λ_{max} (E_{rel}) = 379.4 (0.72), 410.6 (0.31), 437.0 (0.66), 467.0 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 437 nm): λ_{max} (I_{rel}) = 476.4 (1.00), 509.6 (0.66), 547.3 nm (0.20). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437nm/1\ cm}$ = 0.0137, reference: **S-13** with Φ = 1.00): 0.07. MS (FAB^+): *m/z* (%): 1025.9 (16) [M^+ + H], 1024.9 (8) [M^+],843.7 (8), 661.4 (14). HRMS ($C_{67}H_{68}N_4O_6$): Calcd. 1025.5212 [M^+], found 1025.5217 [M^+]; Δ = +0.0004.



2-[5-(Anthracen-9-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (16): *N,N**-Bis(1-hexylheptyl)-*N**-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1',2':3,4:9,10-hexacarboxylic-1',2':3,4:9,10-tris(dicarboximide) (**6**, 100 mg, 95.2 µmol) under argon atmosphere was dissolved in THF (5.0 mL), treated with $PdCl_2(PPh_3)_2$ (15 mg, 13 µmol), CuI (3.2 mg, 17 µmol), PPh_3 (3.4 mg, 13 µmol), then treated with 9-ethynylanthracene (108 mg, 534 µmol), triethylamine (2.5 mL), stirred at 80 °C (bath) for 15 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 800×44 mm, chloroform/ethanol 80:1). Yield 85 mg (78%) red solid, m.p. > 250 °C. R_f -value ($CHCl_3$/EtOH 80:1) = 0.30. IR (ATR): $\tilde{\nu}$ = 2927.3 (w), 2854.9 (w), 1691.2 (s), 1655.7 (s), 1593.5 (s), 1579.5 (m), 1508.0 (w), 1484.0 (w), 1466.7 (w), 1457.4 (w), 1434.8 (w), 1405.8 (m), 1373.8 (m), 1348.9 (s), 1243.7 (s), 1205.0 (m), 1193.4 (m), 1176.3 (m), 1153.5 (w), 1137.6 (w), 1128.0 (w), 1106.0 (w), 1017.9 (w), 973.1 (w), 960.3 (w), 880.2 (w), 860.2 (m), 851.8 (m), 842.0 (m), 811.7 (m), 803.9 (w), 781.6 (w), 765.4 (w), 747.6 (m), 735.6 (s), 679.7 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, ^3J(H,H) = 6.9 Hz, 6 H, 2×CH_3), 1.18–1.42 (m, 16 H, 6×CH_2), 1.85–1.93 (m, 2 H, β-CH_2), 2.21–2.29 (m, 2 H, β-CH_2), 5.15–5.24 (m, 1 H, N–CH), 7.50–7.67 (m, 4 H, 4×$CH_{aromat.}$), 7.99–8.06 (m, 2 H, 2×$CH_{aromat.}$), 8.28 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.44 (s, 1 H, $CH_{aromat.}$), 8.59 (d, ^3J(H,H) = 9.3 Hz,1 H, $CH_{pyridine}$), 8.60–8.66 (m, 8 H, 8×$CH_{perylene}$), 9.09 ppm (d, ^4J(H,H) = 2.1 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 29.2, 31.8, 32.4, 54.8, 90.7, 96.3, 116.0, 121.5, 123.0, 123.4, 123.9, 125.8, 126.4, 126.7, 127.1, 128.7, 128.8, 129.5, 130.0, 131.1, 131.8, 132.8, 134.2, 135.4, 140.9, 148.2, 152.3, 163.4 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 460.0 (24800), 491.4 (54000), 527.8 nm (84600). MS (FAB$^+$): *m/z* (%): 851.0 (100) [M^+ + H], 668.7 (3), 373.4 (4). HRMS ($C_{58}H_{47}N_3O_4$): Calcd. 850.3326 [M^+], found 850.3332 [M^+]; Δ = +0.0006. $C_{58}H_{47}N_3O_4$ (849.36): Calcd. C 81.95, H 5.57, N 4.94; found C 82.13, H 5.48, N 4.75.



***N,N′*-Bis-(1-hexylheptyl)-*N′*-[5-(anthracen-9-ylethynyl) pyridin-2-yl]benzo[*ghi*]perylene-1′,2′:3,4:9,10-hexacarboxylic-1′,2′:3,4:9,10-tris(dicarboximide) (15)**: *N,N**-Bis(1-hexylheptyl)-*N**-(5-iodopyridin-2-yl)benzo[*ghi*]perylen-1',2':3,4:9,10-hexacarboxylic-1',2':3,4:9,10-tris (dicarboximide) (**3**, 100 mg, 95.2 µmol) under argon atmosphere with the exclusion of moisture, triphenylphosphine (2.5 mg, 9.5 µmol), bis(triphenylphosphine)palladiumchloride (6.7 mg, 9.5 µmol) and copper(I)iodide (2.0 mg, 9.5 µmol) were dispersed in triethylamine (2.5 mL), treated with 9-ethynylanthracene (108 mg, 534 µmol) in dry THF (5 mL), stirred at 80 °C (bath) for 15 h, evaporated in vacuo, dispersed in chloroform (50 mL) washed with 2 M aqueous HCl (50 mL) and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation in dimmed light (silica gel 800×44 mm, chloroform and then silica gel 300×44 mm, chloroform; the material is sensitive to photo oxydation). Yield 35 mg (31 µmol, 33%) yellow dye, m.p. > 250 °C. R_f-value (silica gel, $CHCl_3$) = 0.30. IR (ATR): $\tilde{\nu}$ = 2952.3 (w), 2922.6 (m), 2854.8 (m), 2361.3 (w), 2341.2 (w), 1722.6 (s), 1704.6 (s), 1662.1 (s), 1625.9 (w), 1596.1 (m), 1554.7 (w), 1521.0 (w), 1475.9 (m), 1462.7 (m), 1440.9 (w), 1413.8 (m), 1364.3 (s), 1350.0 (s), 1317.6 (s), 1302.2 (s), 1278.4 (m), 1241.3 (m), 1216.9 (m), 1205.1 (m), 1167.8 (m), 1127.7 (w), 1092.0 (w), 1082.1 (w), 1068.2 (w), 1012.7 (w), 965.0 (w), 939.2 (w), 925.5 (w), 891.0 (w), 868.0 (w), 846.1 (w), 836.3 (w), 811.8 (m), 784.4 (w), 765.3 (m), 739.1 (w), 737.2 (m), 697.5 (w), 658.6 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.76–0.92 (m, 12 H, 4×CH_3), 1.17–1.53 (m, 32 H, 16×CH_2), 1.92–2.00 (m, 4 H, 2×β-CH_2), 2.00–2.09 (m, 4 H, 2×β-CH_2), 5.21–5.46 (m, 2 H, 2×N–CH), 7.35–7.79 (m, 4 H, 4×$CH_{aromat.}$), 7.78 (d, ^3J(H,H) = 8.0 Hz, 1 H, $CH_{pyridine}$), 7.87 (d, ^3J(H,H) = 8.1 Hz, 2 H, 2×$CH_{aromat.}$), 8.17 (d, ^3J(H,H) = 8.6 Hz, 1 H, $CH_{pyridine}$), 8.26–8.39 (m, 1 H, 1×$CH_{aromat.}$), 9.01 (s, 1 H, $CH_{pyridine}$), 9.20–9.51 (m, 4 H, 4×$CH_{perylene}$), 10.48 ppm (s, 2 H, 2×$CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 29.3, 29.7, 31.8, 32.5, 90.5, 96.1, 123.0, 123.7, 125.2, 125.8, 127.5, 166.1 ppm. MS (FAB$^+$): *m/z* (%): 1158.3 (0.25) [M^+ + 2 O; photo oxydation], 1126.3 (0.35) [M + H^+], 1082.3 (0.10), 944.1 (0.15), 706.1 (0.10), 628.0 (0.10). HRMS ($C_{75}H_{72}N_4O_6$): Calcd. 1125.5525, found 1125.5530, Δ = + 0.0005.

Acknowledgements

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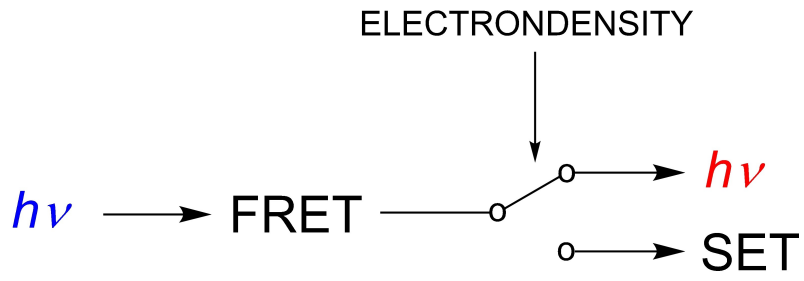

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