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Three Orthogonal Chromophores Operating Independently within the Same Molecule

Heinz Langhals,*,† Maximilian Rauscher,† Jörg Strübe,‡ and
Dietmar Kuck*,‡

*Department of Chemistry, LMU University of Munich,
Butenandtstrasse 13, 81377 Munich, Germany, and Department
of Chemistry, Bielefeld University, Universitätsstrasse 25,
33651 Bielefeld, Germany*

*langhals@lrz.uni-muenchen.de;
dietmar.kuck@uni-bielefeld.de*

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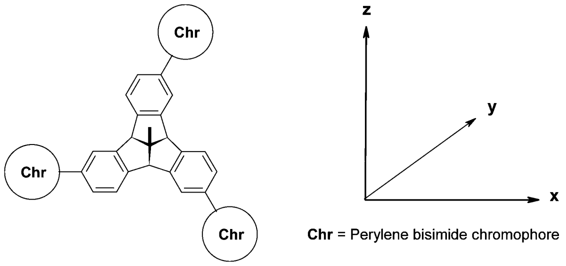
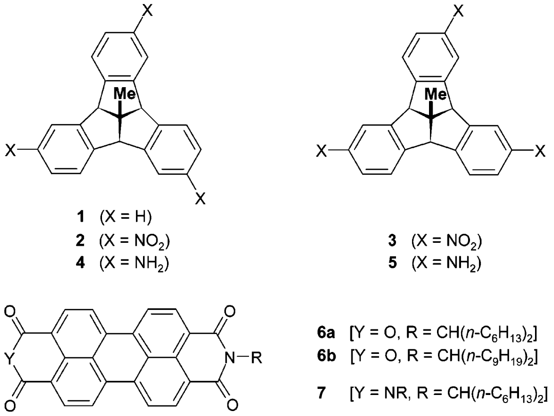


Three perylene bisimide chromophores were arranged orthogonally to each other within the same molecule by appropriate 3-fold coupling to 10-methyltribenzotriquinacene, a rigid C_{3v}-symmetrical framework containing three indane units oriented at right angles in space. The electronic operation of the three chromophores was shown to be independent within the C_3-symmetrical product, and potential applications of this novel molecular setup in molecular electronics are discussed.

Molecular electronics and molecular functional devices are subjects of interest in modern chemistry. Operating elements of well-defined molecular structures and shapes are required for their development. Chromophores[1] are of special interest as functional units because they are interfaces for the interaction between the energy of light and matter and, thus, represent key structures for the majority of functional materials. However, in most of these, one single chromophore is incorporated in each single molecule. The presence of two or more chromophores within each molecule opens an even larger manifold of possibilities because exciton effects,[2−6] energy,[7] and electron[8] transfer processes can take place between the chromophores. However, such exciton interaction prevents independent operation of the chromophores, and due to this type of coupling, insulation such as for macroscopic electronics does not exist on the molecular level.[9,10] Nevertheless, independent operation of two or more chromophores within the same molecule would be of interest for the construction of complex molecular functional units characterized by a very high degree of integration.

The electronic interaction of π-electron systems may be switched off by an orthogonal arrangement of these, but suitable basic structures required for such constructions are rare. However, centropolyindanes,[11−15] bearing up to six mutually fused indane units within their particularly rigid polycyclic molecular frameworks, offer such suitable core scaffolds owing to their "Cartesian" geometry.[12] Exciton interactions between chromophores can be detected by their inducing characteristic alterations of the UV/vis absorption spectra of the individual parent chromophores and, in turn, can be excluded by the absence of the latter.



1 (X = H)
2 (X = NO_2)
4 (X = NH_2)

3 (X = NO_2)
5 (X = NH_2)

6a [Y = O, R = $CH(n\text{-}C_6H_{13})_2$]
6b [Y = O, R = $CH(n\text{-}C_9H_{19})_2$]
7 [Y = NR, R = $CH(n\text{-}C_6H_{13})_2$]

We used the readily accessible framework of tribenzotriquinacene, the *trifuso*-centrotriindane,[10−14,16] as the basic structure for orthogonally arranged chromophores. Specifically,

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† LMU University of Munich.
‡ Bielefeld University.

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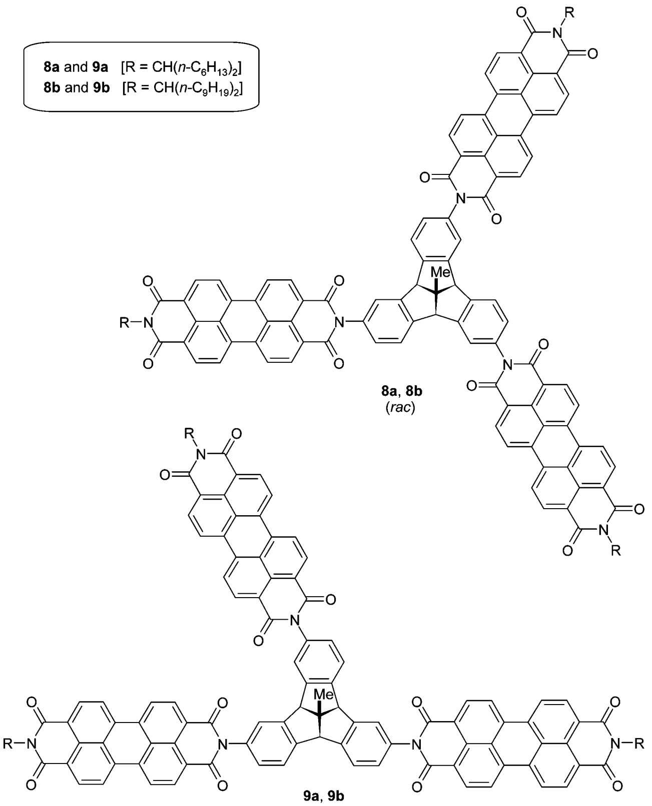
the *centro*-methyl derivative **1**[17] was employed because of its chemical stability and high versability.[11−14,18−22] Owing to the mutually orthogonal orientation of the three indane units of **1**,[11,12,19b] the three chromophores attached to the peripheral positions of the benzene rings would also adopt an orthogonal orientation in space. Nitration of **1** yields a ca. 1:3 mixture of the C_3- and the C_1-symmetrical trinitro derivatives **2** and **3**, respectively, reflecting a random attack of the electrophile at each of the benzene rings.[11,12,23] Reduction of the mixture of racemates gave the corresponding 1:3 mixture of C_3- and C_1-symmetrical triamino derivatives **4** and **5**, respectively.[23] Separation of the constitutional isomers turned out to be difficult in both cases. Therefore, the mixed amines **4** and **5** were condensed[24] with the perylene anhydride imides[25] **6a** and **6b** to form the corresponding isomeric tris(perylene) dyes **8** and **9**. The two lower analogues of these, **8a** and **9a**, could be separated by chromatography, and their structures could be assigned unambiguously by ^{1}H NMR spectroscopy. As expected, the bridgehead protons of the condensed five-membered rings give rise to a singlet in the ^{1}H NMR spectrum of the C_3-symmetrical isomer **8a**, whereas the signals split for **9a** because of its lack of symmetry.

The perylene bisimide chromophore[26,27] is especially suitable for the construction of such trichromophoric dyes not only because of the chemical[28,29] and photochemical[30] persistency but also because there is only one[31] electronic transition in the visible, which is polarized in the direction of the N−N connection line. The energy and the wavelengths, respectively, of this transition are very insensitive to substituents at the nitrogen atoms[26,32] and to solvent effects,[33] which renders the chromophore an ideal probe for the detection of exciton interactions. Moreover, the chromophore exhibits a high fluorescence quantum yield,[34] allowing us to process and monitor the energy of excitation. Problems concerning solubility and high tendencies for aggregation are expected for dyes in the dimension of **8** and **9**. Therefore, the long-chain secondary alkyl substituents[35] (“swallow-tail substituents”) 1-hexylheptyl (**a**) and 1-nonyldecyl (**b**), respectively, were attached as the terminal groups (R) in **8** and **9**. Compound **9a** was obtained directly by column chromatography, whereas the isolation of **8a** required preparative TLC. By contrast, separation of the even better soluble homologues **8b** and **9b** proved to be much more difficult; therefore, the spectra of the mixture of both isomers were recorded.



8a and **9a** [R = CH(n-C_6H_{13})$_2$]
8b and **9b** [R = CH(n-C_9H_{19})$_2$]

8a, **8b**
(*rac*)

9a, **9b**
(*rac*)

The geometries of **8a** and **9a** were quantum chemically calculated (see Figure 1).[36,37] C_3-symmetry was obtained for the chromophores of **8a**, and the transition moments of the chromophores (N−N connection lines) were found to be orthogonal. The calculated distances between the closest nitrogen atoms are about 8.5 Å. This is sufficiently close for exciton interactions. The N−N distance of the two proximal chromophores in **9a** is 6.5 Å and more than 9 Å for the two distal ones; the value of 8.5 Å was again obtained for the medial arrangement similar to that present in **8a**.

The UV/vis absorption spectra of compounds **8** and **9** exhibit the typical vibronic structure of perylene bisimides, as evidenced

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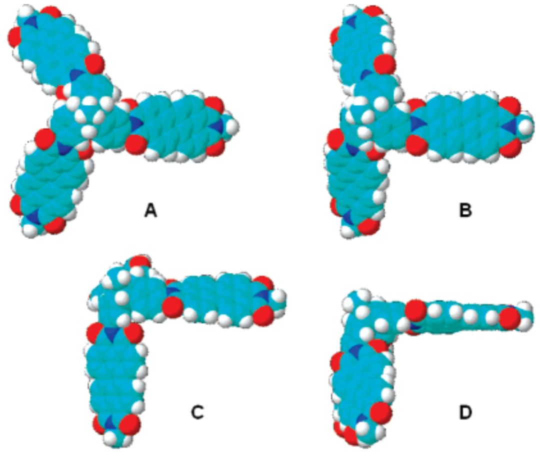

FIGURE 1. Different views on the tribenzotriquinacene-based tris(perylene) core of the C_3-symmetrical dyes **8**, as obtained by AM1 calculation ($R = CH_3$): (A) top view along the molecular axis; (B−D) three views perpendicular to the *x*-axis, the structure being turned counter-clockwise about this axis in two steps of 45°.

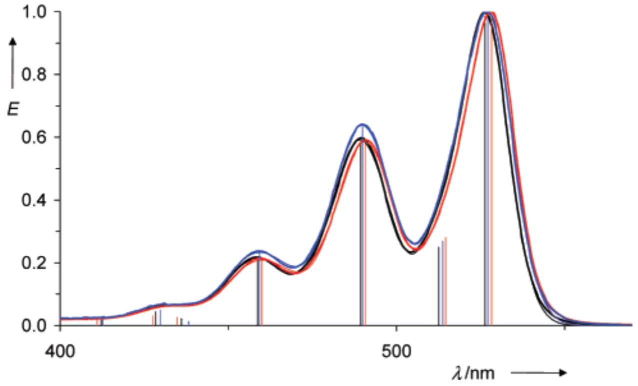

FIGURE 2. Normalized UV/vis spectra of **8a** (red), **9a** (blue), and **7** (black) in chloroform (thick lines) and calculated spectra from Gaussian analysis (thin lines, nearly covered by the thick lines). The bars indicate the calculated positions and intensities of the Gaussian bands.

by comparison with the aliphatically substituted derivative **7** (Figure 2). The spectra of the mixture of **8a** and **9a** and of the mixture of **8b** and **9b** are very similar, although the solubilizing effect of the aliphatic groups R is different. This allows us to rule out any aggregation effects on the spectra and to conclude that the spectra presented in Figure 2 are due to the absorption of isolated molecules.

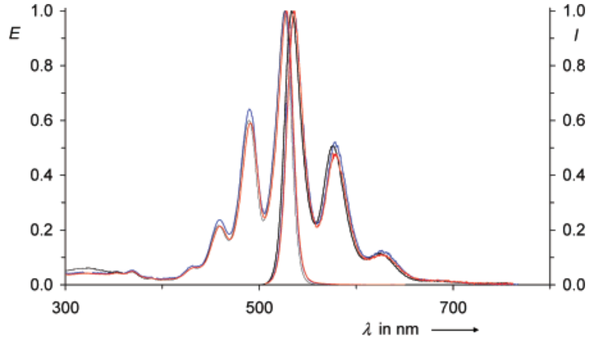

FIGURE 3. Normalized UV/vis absorption (left) and fluorescence (right) spectra of **8a** (red), **9a** (blue), and **7** (black) in chloroform.

The three chromophores in dye **8** are placed orthogonally and, thus, are electronically decoupled. As a consequence, the UV/vis absorption spectrum of **8a** is identical with the spectrum of the monochromophore **7** except for a negligibly small bathochromic shift due to the different substitution at the nitrogen atoms (see Figure 2). A Gaussian analysis[38,39] was performed successfully for the spectra of **8a** and **7** (see Figure 2 and Table 1, Supporting Information). The perfect decoupling of the chromophores in **8** is demonstrated by the very similar pattern of Gaussian functions. By contrast, there is only one pair of orthogonal chromophores in **9**; the two proximal chromophores include an angle of less than 90° for the transition moment (N−N connection lines), giving rise to a H-type interaction.[40,41] The UV/vis spectra of **9** are appreciably altered by this interaction (cf. ref 26). As a consequence, the more hypsochromic vibration bands become more prominent (see the blue lines in Figure 2 and cf. ref 42). There are notable differences between the UV/vis spectra of **8a** and **9a**, although the dimensions of the molecules are very similar as is indicated by the very similar chromatographic properties.

The fluorescence quantum yields of both **8** and **9** are close to unity. The fluorescence spectra of **8a**, **9a**, and **7** are very similar and exhibit the same tendency as the UV/vis spectra (see Figure 3). This further confirms that the chromophores in **8** operate independently from each other. Moreover, it corroborates the finding that the tris(perylene) dyes **8** and **9** exist as isolated, nonaggregated molecules in solution.

The concept of orthogonally arranged chromophores offers many novel possibilities because chromophores are important building blocks for molecular electronics and molecular processing. Thus, structures such as **8** may be points of insulation where different functional unities are operating independently from each other. A slight bending of such a structure will switch on the interaction of the chromophores and thus may operate as a reversible molecular switch. The manifold of the tribenzoquinacenes and their congeners, such as tetrabenzo[5.5.5.5]-fenestranes (fenestrindanes[11−15]), and their facile preparation and functionalization are good prerequisites for the development of complex molecular electronics on the basis of centropolyindanes.

Experimental Section

2,2′,2′′-(4b,8b,12b,12d-Tetrahydro-12d-methyldibenzo[2,3:4,5]-pentaleno[1,6-*ab*]indene-2,6,10-triyl)tris-{9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone} (8a) and 2,2′,2′′-(4b,8b,12b,12d-Tetrahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene-2,6,11-triyl)tris-{9-(1-hexylheptyl)-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone} (9a). 9-(1-Hexylheptyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]-isoquinoline-1,3,8,10-tetraone (**6a**, 200 mg, 0.349 mmol), a ca. 1:3 mixture of 2,6,10-triamino-4b,8b,12b,12d-tetrahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (**4**)[11,12,23] and 2,6,11-triamino-4b,8b,12b,12d-tetrahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (**5**)[11,12,23] (26 mg, 77 μmol), imidazole (1.0 g), and the quantity of a micro spatulum of $Zn(OAc)_2 \cdot 2\ H_2O$ were heated for 3 h under argon at 140 °C. The product mixture was cooled to room temperature, diluted with ethanol (15 mL) and 2 M

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HCl (80 mL), collected by vacuum filtration (D4 glass filter), dried in air, purified by column separation (800 mL silica gel, chloroform/ethanol 40:1), and further purified by column separation with fine silica (1000 mL silica, chloroform/ethanol 20:1) to obtain a mixture of **8a** and **9a** as the first fraction and pure **9a** as the second one. The first fraction was further purified by preparative TLC (silica gel: TLC aluminum sheets 20 × 20 cm silica gel 60 F_{254} with concentrating zone, chloroform) to isolate pure **8a**: yield 9 mg (4%) of **8a** as a red powder; R_f 0.08 (silica gel, $CHCl_3$/EtOH = 40:1); ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) δ 0.82 (t, $^3J = 6.9$ Hz, 18 H), 1.21−1.36 (m, 48 H), 1.81−1.92 (m, 9 H), 2.20−2.29 (m, 6 H), 4.69 (s, 3 H), 5.15−5.22 (m, 3 H), 7.21−7.24 (m, 3 H), 7.51 (s, 3 H), 7.61−7.63 (m, 3 H), 8.66−8.76 (m, 24 H); ^{13}C NMR (151 MHz, $CDCl_3$, TMS, 25 °C) δ 14.2, 22.8, 27.2, 29.4, 29.9, 32.0, 32.6, 55.0, 63.6, 105.0, 123.3, 123.5, 123.5, 123.7, 132.2, 134.7, 135.3, 145.9, 146.4, 163.9; MS (MALDI-TOF at $M/\Delta M \approx$ 1500, matrix DCTB/$CHCl_3$) m/z 2006.5 (maximum of the unresolved peak envelope); MS (MALDI-FT-ICR at $M/\Delta M > 20\,000$, matrix DCTB/$CHCl_3$) m/z 2003.8857 (52, $[M - H]^+$), 2004.8888 (81, $[M]^{\bullet +}$ and $[^{13}C_1]$-$[M - H]^+$), 2005.8956 (100), 2006.9016 (91), 2007.9066 (58), 2008.9113 (27), 2009.9168 (11), 2010. 9176 (3); accurate mass of the $[M - H]^+$ ion ($C_{134}H_{119}N_6O_{12}{}^+$), calcd 2003.88805, found 2003.88569 (see above); UV/vis ($CHCl_3$, 25 °C) λ_{max} (E_{rel}) 459.4 (0.21), 490.8 (0.59), 528.2 nm (1.00); fluorescence λ_{max} (I_{rel}) 536.3 (1.00), 579.3 (0.48), 626.0 nm (0.11); fluorescence quantum yield ($CHCl_3$, $\lambda_{exc} = 490$ nm) $E_{490\ nm} = 0.0147\ cm^{-1}$, reference: **7** with $\Phi = 1.00$) $\Phi = 1.0$; GPC (THF, flow rate 2.00 mL/min, 40 °C) $M_p = 2700$, $PD = 1.04$; yield 28 mg (12%) of **9a** as a red powder; R_f 0.05 (silica gel, $CHCl_3$/EtOH 60:1); ^1H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.78−0.89 (m, 18 H), 1.17−1.35 (m, 48 H), 1.82−1.91 (m, 9 H), 2.17−2.23 (m, 6 H), 4.67 (s, 1 H), 4.70 (s, 1 H), 4.76 (s, 1 H), 5.12−5.22 (m, 3 H), 7.16 (d, $^3J = 8.1$ Hz, 1 H), 7.40−7.43 (m, 4 H), 7.50 (s, 1 H), 7.58 (d, $^3J = 8.1$ Hz, 1 H), 7.79−7.82 (m, 2 H), 8.40−8.69 (m, 24 H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C) δ 14.2, 14.3, 22.7, 22.8, 27.1, 27.2, 27.9, 29.4, 29.5, 29.9, 31.9, 32.0, 32.5, 55.1, 105.0, 123.2, 123.6, 131.7, 134.6, 134.7, 145.8, 146.0, 163.5; UV/vis ($CHCl_3$, 25 °C) λ_{max} (ϵ) 458.1 (53100), 489.4 (143700), 526.6 nm (223000); fluorescence λ_{max} (I_{rel}) 536.3 (1.00), 578.5 (0.52), 626.5 nm (0.12); fluorescence quantum yield ($CHCl_3$, $\lambda_{exc} = 490$ nm, $E_{490\ nm} = 0.0191\ cm^{-1}$, reference **7** with $\Phi = 1.00$) $\Phi = 1.0$; GPC (THF, flow rate 2.00 mL/min, 40 °C) $M_p = 2200$, $PD = 1.03$; MS (FAB+), m/z (relative intensity, %) 2006 ($M^{\bullet +}$, 0.8). Mixture of the isomers **8a** and **9a**: IR (ATR) $\tilde{\nu}$ (cm^{-1}) 3072 w, 2922.6 s, 2853.2 m, 1697.2 s, 1655.5 vs, 1593.1 s, 1577.8 m, 1505.4 w, 1487.5 w, 1454.8 w, 1432.0 w, 1404.7 m, 1337.2 vs, 1249.8 m, 1172.3 m, 1135.6 w, 1119.9 w, 1107.3 w, 964.0 w, 851.2 w, 829.9 w, 809.2 m, 789.8 w, 744.7 m, 640.0 w; GPC (THF, flow rate 2.00 mL/min, 40 °C) $M_p = 2600$, $PD = 1.17$. MS (FAB+), m/z (relative intensity, %) 2006 ($M^{\bullet +}$, 3).

2,2′,2″-(4b,8b,12b,12d-Tetrahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene-2,6,10-triyl)tris-{9-(1-nonyldecyl)-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone} (8b) and 2,2′,2″-(4b,8b,12b,12d-Tetrahydro-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene-2,6,11-triyl)tris-{9-(1-nonyldecyl)-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone} (9b). 9-(1-Nonyldecyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (**6b**, 155 mg, 0.236 mmol), the mixture of the isomeric triaminotribenzotriquinacenes **4** and **5** (19 mg, 53 μmol), imidazole (1.0 g), and the quantity of a micro spatulum of $Zn(OAc)_2 \cdot 2\ H_2O$ were allowed to react as is described for **8a** and **9a**. The products were separated by column chromatography (800 mL silica gel, chloroform/ethanol 40:1) and further purified by column separation with fine silica (1000 mL silica, chloroform/ethanol 40:1) to obtain a mixture of **8b** and **9b**: yield 14 mg (12%), as a dark red powder; R_f 0.10 (silica gel, $CHCl_3$/EtOH 40:1); IR (ATR) $\tilde{\nu}$ (cm^{-1}) 3068.6 w, 2921.4 vs, 2851.8 s, 1697.9 s, 1655.9 vs, 1593.0 s, 1577.4 m, 1505.0 w, 1488.2 w, 1454.9 w, 1431.9 w, 1404.0 m, 1338.3 vs, 1253.8 m, 1194.5 w, 1173.0 w, 1088.8 w, 1017.2 w, 964.2 w, 851.3 w, 808.6 m, 793.7 m, 744.4 m, 662.2 w, 643.1 w, 634.0 w, 615.4 w; ^1H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 0.78−0.84 (m, 18 H), 1.16−1.28 (m, 84 H), 1.85−1.97 (m, 9 H), 2.17−2.29 (m, 6 H), 4.69−4.78 (m, 3 H), 5.09−5.20 (m, 3 H), 7.11−7.13 (m, 1 H), 7.46−7.64 (m, 6 H), 7.93−8.68 (m, 26 H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C, TMS) δ 14.3, 22.8, 27.1, 27.4, 27.9, 29.4, 29.5, 29.7, 29.8, 32.0, 32.1, 32.4, 55.0, 55.1, 62.8, 63.5, 63.7, 122.9, 123.4, 124.2, 124.6, 124.8, 125.1, 125.8, 126.0, 126.4, 128.8, 129.1, 129.2, 129.3, 129.6, 131.2, 131.8, 134.3, 134.5, 134.8, 145.8, 146.1, 146.2, 146.3, 146.6, 163.6; UV/vis ($CHCl_3$) λ_{max} (E_{rel}) 459.2 (0.24), 490.0 (0.64), 527.2 nm (1.00); fluorescence ($CHCl_3$) λ_{max} (I_{rel}) 535.5 (1.00), 578.0 (0.53), 626.0 nm (0.12); fluorescence quantum yield ($CHCl_3$, $\lambda_{exc} = 488$ nm, $E_{488\ nm} = 0.0281\ cm^{-1}$, reference **7** with $\Phi = 1.00$) $\Phi = 1.0$; GPC (THF, flow rate 2.00 mL/min, 40 °C) $M_p = 5665$, $PD = 1.11$. MS (FAB+), m/z relative intensity (%) 2258 ($M^{\bullet +}$, 0.2).

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **8a** and **9a** and of **8b**/**9b** (mixture); Gaussian analysis data of the UV/vis spectra of **8a**, **9a**, and **7**; absolute energies and atom coordinates of structures **8** (R = CH_3) and **9** (R = CH_3). This material is available free of charge via the Internet at http://pubs.acs.org.

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