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Axially Chiral Bichromophoric Fluorescent Dyes

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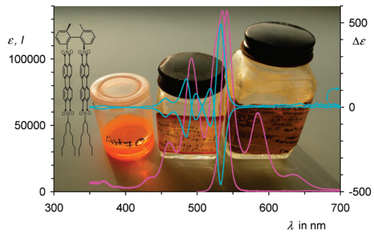
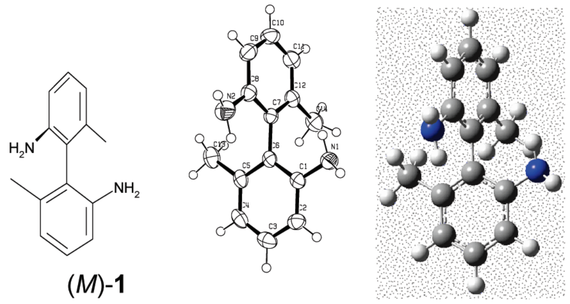


A new life for Kurt Mislow's authentic amines: Diaminobiphenyls were applied as the framework materials for the synthesis of axially chiral bichromophoric systems with strong CD and CPL effects.

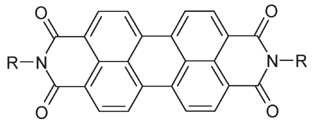
Axially chiral diamino binaphtyls and biphenyls were important compounds for monitoring steric effects and noncovalent interactions some 50 years ago. Kurt Mislow prepared axially chiral amines in pioneering synthesis on the basis of bi-*o*-tolyl and 1,1′-binaphthyl amines.[1] On the other hand, these amines form ideal chiral frameworks for the construction of multichromophoric devices with restricted orientation of electronic transition moments where exciton interactions, charge, and energy transfer become important.

The bi-*o*-tolyl derivatives are of special interest for such applications because of their hypsochromic light absorption avoiding interference with attached chromophores. We investigated the geometry of (*M*)-**1** by means of X-ray crystal structure analysis. The two phenyl groups are nearly orthogonal including an interplanar angle of 85.97(10)°, a dihedral angle of the nitrogen-attached carbon atoms of −93.95(0)°, and an interconnecting single bond of 1.493(3) Å; see Figure 1. The packing of **1** is dominated by weak N−H···N and N−H···C contacts leading to strands along *a*. The structure of **1** was additionally quantum chemically calculated with the DFT method starting with the geometry from the X-ray crystal structure analysis and gave a dihedral angle of −103°; this corresponds to the underestimation[2] of steric interactions by this method. Better results concerning the crystal structure of **1** were obtained with the semiempirical AM1 method where −94° was found close to the experimental value.



(*M*)-**1**

FIGURE 1. From left to right: chemical structure, X-ray crystal structure and calculated (DFT, B3LYP) structure of (*M*)-**1**.



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Perylene-3,4:9,10-tetracarboxylic bisimides[3] (**2**) are suitable chomophores for the construction of bichromophoric arrangements (dyads) because there is only one electronic transition in the visible[4] helping the interpretation of optical effects. This very pure $\pi-\pi^*$ transition in **2** is polarized along the long molecular axis and is ideal for studying exciton interactions. High fluorescent quantum yields close to unity, high molar absorptivities, and chemical and photochemical stability are further advantages of the chromophore. We started for the orientation of the chromophores **2** with the anhydride[5] **3** where the long-chain *sec*-alkyl group 1-hexylheptyl renders the material soluble and condensed it with Mislow's 2,2′-diamino-4,4′-dimethylbiphenyl[1] (**1**) as the framework because it exhibits a high barrier for racemization so

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(1) (a) Mislow, K.; Rutkin, P.; Lazarus, A. K. *J. Am. Chem. Soc.* **1957**, *79*, 2974–2975. (b) Jones, W. M.; Wilson, J. W. *Tetrahedron Lett.* **1965**, *21*, 1587–1592. Mislow, K. *Angew. Chem.* **1958**, *70*, 638–689. (c) The author J.S.S. supports the technical aspects of this work fully but disagrees with the use of terminology like "axial chirality"; see: Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319−3328. Cozzi, F.; Siegel, J. S. *Org. Biomol. Chem.* **2005**, *3*, 4296−4298. The author H.L. emphasizes that terms such as "axial chirality" or the "asymmetric carbon atom" are no more than useful chemical models for helical arrangements of electrons induced by the nuclear framework. Elements of symmetry of polyatomic molecules in solution are in no way verified in reality because of zero point vibrations and many other effects where, for example, phenomenologically achiral molecules form either fast equilibria of racemization or reach states with rotary alternating axes.

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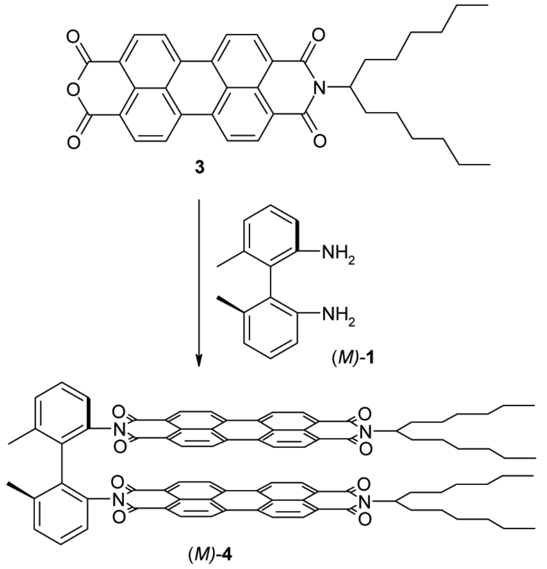
DOI: 10.1021/jo102254a



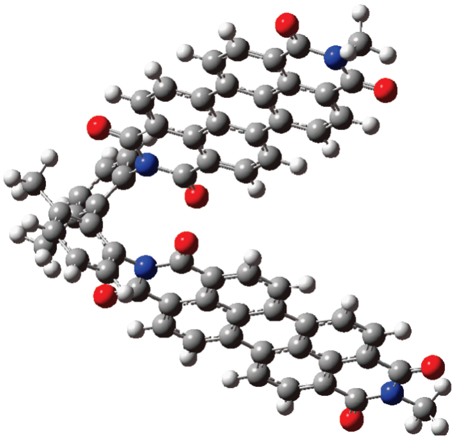


FIGURE 2. Calculated structure (DFT, B3LYP) for the *N*-methyl derivative of (*M*)-**4**.

that both enantiomers (*P*)-**4** and (*M*)-**4** could be obtained as stable compounds. The barrier of entiomeric stability was tested for **4** in the solvent Dowtherm A[6] where no racemization was found at 200 °C for 30 h; the previously reported[3,7] binapthyl derivatives exhibited also no racemization under the same condition. One could estimate a lower limit of the remarkably high free enthalpy of racemization of > 137 kJ·mol^{-1}. Furthermore, there was no chemical degradation of the aliphatic side chains. As a consequence, we tested the chemical stability by means of DTA and thermogravimetry at even more elevated temperatures and did not find decomposition until 380 °C. 26.9% of mass was lost between 380 and 450 °C corresponding to the loss of the aliphatic *N* substituents. The aromatic system proved to be stable until 520 °C.

The geometry of (*M*)-**4** was quantum chemically calculated where a slightly absolutely smaller dihedral angel was obtained: AM1 −91° and DFT, B3LYP −83°; see Figure 2. This may be a consequence of the interaction of the two chromophores.

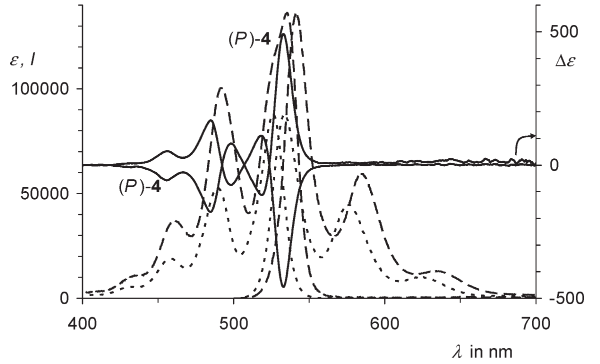


FIGURE 3. UV/vis absorption, fluorescence (left scale) and CD spectra (right scale, normal lines) in chloroform. Dashed lines: Absorption (left) and fluorescence (right) spectra of (*M*)-**4**; the spectra of (*P*)-**4** are identical. Dotted lines: Spectra of **1a** (R = 1-hexylheptyl) for comparison. Positive CD effect for (*P*)-**4** and negative for (*M*)-**4**.

The very small dimethyl biphenyl linker in **4** is of special advantage compared with the previously published binaphthyl spacer[7] because it does not contribute to light absorption in the visible and the UVA. As a consequence, there is no interference with the light absorption of the perylene chromophore.

The UV/vis absorption spectrum of **4** is strongly structured and exhibits about two times the absorptivity of **2** except for the most bathochromic band where exciton interaction causes a shoulder and the molar absorptivity is diminished compared with **2**. **4** exhibits strong, structured fluorescence being approximately mirror-type concerning the absorption spectrum (Figure 3).

Fluorescence quantum yields close to unity were found for both (*P*)-**4** and (*M*)-**4**, respectively. There is a precisely monoexponential decay of fluorescence. The fluorescence lifetime of 4.54 ns is slightly larger than that for other perylene dyes of about 3.9 ns;[3] this corresponds to the comparably smaller molar absorptivity of **4** because 180 000 is expected for two perylenetetracarboxylic bisimide chromophores, whereas 135 000 was found for **4**. Strong mirror-type CD effects were observed for the enantiomers (*P*)-**4** and (*M*)-**4**, respectively, with Δε of some ±500. These are dominated by exciton interactions because of the very pure $\pi-\pi^*$ transition in the perylene chromophores causing as well only a vanishing CD contribution as the hypsochromic absorption by the linker. The sign of the exciton interaction corroborates the reported configuration of the starting biphenyl amines with respect to the direction of the transition dipole in the perylene biscarboximides.

$$g = \frac{2(\Gamma_{\text{left}} - \Gamma_{\text{right}})}{\Gamma_{\text{left}} + \Gamma_{\text{right}}} \qquad (1)$$

The chirally arranged chromophores emit chiral fluorescent light where about 0.1% of the fluorescence was circularly polarized with a comparably strong mirror-type CPL effect for both enantiomers (Figure 4). Slight deviations from the complete symmetry are caused by asymmetries of the experimental setup. Interestingly, there are no strong flips in sign of the CPL spectra as was observed for the CD spectra in

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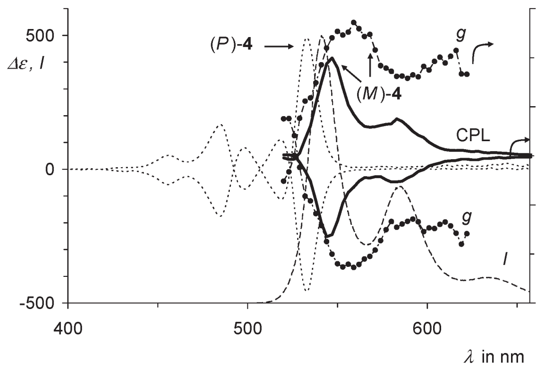

FIGURE 4. Fluorescence CPL spectra ($\Delta I/I$, thick lines, right scale, stretched by a factor 2 for better visibility) and *g* values (-•-) of (*M*)-**4** (upper lines) and (*P*)-**4** (lower lines) compared with the CD spectra (dotted lines, left scale; see Figure 2) and the fluorescence spectrum of (*P*)-**4** (dashed line and arbitrary units).

the absorption. The *g* value according to eq 1, where Γ_{right} and Γ_{left} respectively mean the intensity of right and left circularly polarized light, is in the order of 0.2% (cf. Figure 3). Chiral effects in fluorescence can be attributed to the exciton interactions, where both CPL and *g* are in the expected range[8,9] for a setup as in **4**.

We conclude that atropisomeric diamino biphenyls, initially introduced for basic investigations of steric effects by Kurt Mislow, proved to form interesting and powerful frameworks for the development of novel chiral materials with unusual optical properties. One could imagine the construction of a chiral laser-type light amplifier with compounds such as **4** amplifying chiroptical properties.

Experimental Section

CPL Measurements. The previously described[10] setup was applied for CPL.

(*P*)-4: 9-(1-Hexylheptyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra-[2,1,9:*def*]isoquinoline-1,3,8,10-tetraone (**2**, 85 mg, 0.15 mmol), (*P*)-(+)-6,6′-dimethylbiphenyl-2,2′-diamine (15 mg, 0.07 mmol), and imidazole (3 g) were heated under argon atmosphere at 140 °C for 4 h, allowed to cool, still warm precipitated with 2 M aqueous HCl (20 mL), collected by vacuum filtration (D4 glass filter), washed with 2 M HCl and distilled water, dried in air at 110 °C for 16 h, and purified by column separation (silica gel, chloroform/ethanol 50:1). Yield 60 mg (65%) of red solid, mp > 300 °C. R_f (silica gel, chloroform/ethanol 20:1) 0.78. IR (ATR) ν 2921.9 (s), 2855.2 (m), 2361.5 (m), 2337.6 (m), 1697.4 (s), 1656.6 (vs), 1592.0 (vs), 1576.4 (s), 1505.8 (w), 1455.7 (w), 1492.2 (w), 1403.9 (m), 1338.1 (vs), 1250.3 (m), 1172.8 (m), 1124.5 (w), 1105.6 (w), 963.5 (w), 850.8 (w), 809.2 (m), 774.4 (w), 745.1 (w), 681.9 (w), 668.0 cm^{-1} (w). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C, TMS) δ 0.74−0.82 (m, 6 H, 2 × CH$_3$), 1.02−1.09 (m, 6 H, 2 × CH$_3$), 1.12−1.80 (m, 32 H, 16 × CH$_2$), 2.22−2.38 (m, 4 H, β-CH$_2$), 2.34−2.56 (m, 4 H, β-CH$_2$), 2.73 (s, 6 H, 2 × CH$_3$), 5.25−5.36 (m, 2 H, NCH), 7.18 (d, ^3J(H,H) = 6.5 Hz, 2 H, 2 × CH$_{\text{aromat.}}$), 7.39 (t, ^3J(H,H) = 7.5 Hz, 2 H, 2 × CH$_{\text{aromat.}}$), 7.79 (d, ^3J(H,H) = 6.8 H, 2 H, 2 × CH$_{\text{aromat.}}$), 8.20−8.79 ppm (m, 16 H, 16 × CH$_{\text{perylene}}$). ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C, TMS) δ 14.0, 14.3, 20.5, 22.5, 22.9, 26.9, 27.0, 27.4, 27.6, 29.2, 29.5, 29.7, 31.7, 32.0, 32.9, 33.1, 122.5, 123.0, 124.0, 124.7, 125.9, 126.0, 127.1, 128.5, 129.2, 130.2, 131.4, 132.3, 134.1, 134.4, 134.5, 134.8, 135.9, 141.7, 162.9, 163.8, 164.6 ppm. UV/vis (CHCl$_3$) $\lambda_{\max}$ (ε) 461.3 (36400), 492.1 (100400), 535.7 nm (134500). Fluorescence (CHCl$_3$) $\lambda_{\max}$ (I_{rel}) 542.0 (1.00), 585.0 (0.44), 635.0 nm (0.10). Fluorescence quantum yield (CHCl$_3$, λ_{exc} = 585 nm, $E_{585\text{ nm}/1\text{ cm}}$ = 0.0155, reference: **1** with Φ = 1.00) 1.00. MS (FAB$^+$) *m*/*z* (%) 1323.6 (0.6) [M^+ + H], 1322.6 (0.3) [M^+]. HRMS (C$_{87}$H$_{81}$N$_4$O$_8$) calcd *m*/*z* 1322.6133, found *m*/*z* 1322.6117; Δ = +0.0016. Anal. Calcd for C$_{87}$H$_{81}$N$_4$O$_8$ (1322.6): C 79.85, H 6.24, N 4.23. Found: C 79.56, H 6.33, N 4.16.

(*M*)-4: 9-(1-Hexylheptyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra-[2,1,9:*def*]isoquinoline-1,3,8,10-tetraone (**2**, 284 mg, 0.495 mmol), (*M*)-(−)-6,6′-dimethylbiphenyl-2,2′-diamine (50.0 mg, 0.236 mmol), and imidazole (5 g) were allowed to react and purified as was described for (*P*)-**4**. Yield 201 mg (65%) of red solid, mp > 300 °C. R_f (silica gel, chloroform/ethanol 20:1) 0.78. IR (ATR) ν 2921.9 (s), 2855.2 (m), 2361.5 (m), 2337.6 (m), 1697.4 (s), 1656.6 (vs), 1592.0 (vs), 1576.4 (s), 1505.8 (w), 1455.7 (w), 1492.2 (w), 1403.9 (m), 1338.1 (vs), 1250.3 (m), 1172.8 (m), 1124.5 (w), 1105.6 (w), 963.5 (w), 850.8 (w), 809.2 (m), 774.4 (w), 745.1 (w), 681.9 (w), 668.0 cm^{-1} (w). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C, TMS) δ 0.74−0.82 (m, 6 H, 2 × CH$_3$), 1.02−1.11 (m, 6 H, 2 × CH$_3$), 1.12−1.88 (m, 32 H, 16 × CH$_2$), 2.22−2.39 (m, 4 H, β-CH$_2$), 2.35−2.49 (m, 4 H, β-CH$_2$), 2.70 (s, 6 H, 2 × CH$_3$), 5.26−5.33 (m, 2 H, NCH), 7.16 (d, ^3J(H,H) = 6.5 Hz, 2 H, 2 × CH$_{\text{aromat.}}$), 7.37 (t, ^3J(H,H) = 7.5 Hz, 2 H, 2 × CH$_{\text{aromat.}}$), 7.75 (d, ^3J(H,H) = 6.8 H, 2 H, 2 × CH$_{\text{aromat.}}$), 8.20−8.79 ppm (m, 16 H, 16 × CH$_{\text{perylene.}}$). ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C, TMS) δ 14.0, 14.3, 20.5, 22.5, 22.9, 26.9, 27.0, 27.4, 27.6, 29.2, 29.5, 29.7, 31.7, 32.0, 32.9, 33.1, 122.5, 123.0, 124.0, 124.7, 125.9, 126.0, 127.1, 128.5, 129.2, 130.2, 131.4, 132.3, 134.1, 134.4, 134.5, 134.8, 135.9, 141.7, 162.9, 163.8, 164.6 ppm. UV/vis (CHCl$_3$) $\lambda_{\max}$ (ε) 461.3 (36400), 492.1 (100400), 535.7 nm (134500). Fluorescence (CHCl$_3$) $\lambda_{\max}$ (I_{rel}) = 542.0 (1.00), 585.0 (0.44), 635.0 nm (0.10). Fluorescence quantum yield (CHCl$_3$, λ_{exc} = 585 nm, $E_{585\text{ nm}/1\text{ cm}}$ = 0.0155, reference: **1** with Φ = 1.00) 1.00. MS (FAB$^+$) *m*/*z* (%) 1323.1 (0.8) [M^+ + H], 1322.1 (0.5) [M^+]. HRMS (C$_{87}$H$_{81}$N$_4$O$_8$) calcd *m*/*z* 1322.6133, found *m*/*z* 1322.6228; Δ = +0.0095. Anal. Calcd for C$_{87}$H$_{81}$N$_4$O$_8$ (1322.6): C 79.85, H 6.24, N 4.23. Found: C 79.47, H 6.26, N 4.15.

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Supporting Information Available: Crystallographic data of (*M*)-**1**, ^{1}H NMR and ^{13}C NMR of compounds (*M*)-**1**, (*P*)-**4**, and (*M*)-**4**, the measurement of the fluorescence lifetime of (*M*)-**4**, stability of the configuration of (*P*)-**4**, and the thermal stability of (*P*)-**4** by DTA (differential thermoanalysis) and TGA (thermogravimetry). This material is available free of charge via the Internet at http://pubs.acs.org.

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