Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting information

Excited-state properties of chiral [4]helicene cations

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Synthesis of HelOH

rac-**HelOH** or *Rac*-5,9-bis-(2-hydroxyethyl)-1,13-dimethoxy-5,9-dihydroquinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate salt: At 25 °C, ethanolamine (5.98 g, 98.0 mmol) was added to a solution of tris(2,6-dimethoxyphenyl)carbenium tetrafluoroborate (2.00 g, 3.9 mmol) in NMP (25 mL). The reaction mixture was heated at 110 °C for 1h. Then, NMP and the non-reacted ethanolamine were distilled under reduced pressure (110°C, 15 mmHg). The residual green oil was washed with Et_2O (~25 mL) to afford a precipitate, which was filtered over a Büchner funnel and collected. The titled compound was further purified by (i) dissolution of the crude product in CH_2Cl_2 and (ii) selective precipitation by addition of Et_2O affording the titled compound **1c** (1.68 g, 3.33 mmol, 85%). **^{1}H NMR** (CD_3CN, 400 MHz) δ 8.08 (t, ^3J = 8.6 Hz, 1H), 7.86 (t, ^3J = 8.3 Hz, 2H), 7.66 (d, ^3J = 8.6 Hz, 2H), 7.53 (d, ^3J = 8.8 Hz, 2H), 6.89 (d, ^3J = 8.1 Hz, 2H), 4.84-4.77 (m, 2H), 4.67-4.59 (m, 2H), 4.13 (m, 4H), 3.71 (s, 6H), 3.31 (s, br, 2H); **^{13}C NMR** (CD_3CN, 100 MHz) δ 160.5 (C), 143.9 (C), 143.7 (C), 140.3 (C), 137.8 (CH), 137.0 (CH), 120.3 (C), 113.9 (C), 109.0 (CH), 106.7 (CH), 103.9 (CH), 59.3 (CH_2), 56.5 (CH_3), 52.4 (CH_2); **m.p.** 280 °C; **IR** 3530, 2947, 1605, 1580, 1500, 1470, 1344, 1254, 1150, 1045, 765; **UV/VIS** (CH_2Cl_2, 9.91 x 10^{-6} M, λ_{max} (log ε)) 617 (4.26), 442 (3.92), 312 (4.77), 284 (4.48), 262 (4.51), 242 (4.46), 227 (4.57); **MS** (ESI+, m/z) 417.4.

Rac-5,9-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-1,13-dimethoxy-5,9-dihydroquinolino[2,3,4-*kl*]acridin-13b-ylium tetrafluoroborate salt: Under argon, *rac*-**HelOH** (2.00g, 3.96 mmol, 1 equiv.) was dissolved in 15 mL of dry DMF, in the presence of imidazole (3.24g, 47.6 mmol, 12 equiv.). To this solution, *tert*-butylchlorodimethylsilane (TBSCl) was added (3.59g, 6 equiv.) and the medium was stirred for 24h at 25 °C. The crude mixture was then quenched with water and extracted 3 times with CH_2Cl_2. The aqueous layers were washed with brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The blue-green gummy compound collected was then purified by chromatography over silica gel (20 x 0.5 cm, CH_2Cl_2/MeOH 95:5) to afford the titled compound (1.89 g, 65% yield). **m.p.** 227.9-228.5 °C; $\boldsymbol{R_f}$ (CH_2Cl_2/MeOH (98:2)) = 0.38; **^{1}H NMR** (CD_3CN, 400 MHz) δ 8.09 (t, ^3J = 8.6 Hz, 1H), 7.84-7.76 (m, 4H), 7.60 (d, ^3J = 9.1 Hz, 2H), 6.90 (d, ^3J = 8.1 Hz, 2H), 5.03-4.96 (m, 2H), 4.92-4.82 (m, 2H), 4.32-4.15 (m, 4H), 3.67 (s, 6H), 0.53 (s, 18H), –0.31 (s, 6H), –0.35 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.7 (C), 143.0 (C), 139.5 (C), 137.3 (CH), 136.5 (CH), 113.5 (C),108.3 (CH), 106.4 (CH), 103.0 (CH), 60.5 (CH_2), 55.8 (CH_3), 25.8 (CH_3), 5.4 (CH_3); **IR** 3530, 2947, 2896, 2850, 1605, 1580, 1557, 1500, 1470, 1344, 1254, 1150, 1045,813, 765; **UV/VIS** (CH_2Cl_2, 9.55 x 10^{-6} M, λ_{max} (log ε)) = 618 (4.10), 445 (3.78), 312 (4.60), 284(4.33); **MS** (ESI+, m/z) 646.0.

(–)-(*R*,*M*)-13b-Methanesulfinyl-*p*-tolyl-1,13-dimethoxy-5,9-bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-9,13b-dihydro-5*H*-5,9-diaza-naphtho-[3,2,1-*de*] anthracene: Synthesized (410 mg, 45% yield) using previously reported conditions[1,2] starting from 0.2 mmol of the racemic substrate. This diastereomer corresponds to the most eluted fraction (SiO_2 (20 x 0.5 cm), Et_2O/Pentane (60:40), R_f (Et_2O) = 0.92). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.19 (dd, ^3J = 7.8 Hz, ^3J = 7.6 Hz, 2H), 7.09-7.02 (m, 3H), 6.96 (d, ^3J = 8.1 Hz, 2H), 6.86 (d, ^3J = 8.3 Hz, 1H), 6.75 (d, ^3J = 8.1 Hz, 1H), 6.70 (d, ^3J = 8.6 Hz, 2H), 6.64 (d, ^3J = 8.3 Hz, 1H), 6.45 (d, ^3J = 8.1 Hz, 1H), 6.30 (d, ^3J = 8.1 Hz, 1H), 4.26-4.21 (m, 2H), 4.13-3.92 (m, 7H), 3.55 (d, ^2J = 12.1 Hz, 1H), 3.53 (s, 3H), 3.29 (s, 3H), 2.29 (s, 3H), 0.93 (s, br, 18H), 0.11 (s, br, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 160.4 (C), 157.6 (C), 143.8 (C), 143.6 (C), 142.5 (C), 141.0 (C), 140.1 (C), 138.9 (C), 129.2 (CH), 128.7 (CH), 127.7 (CH), 126.3 (CH), 124.3 (CH), 116.5 (C), 111.4 (C), 110.9 (C), 107.6 (CH), 106.3 (CH), 106.2 (CH), 106.1 (CH), 105.6 (CH), 101.6 (CH), 68.0 (CH_2), 60.3 (CH_2), 59.8 (CH_2), 56.1

(CH_3), 54.7 (CH_3), 49.6 (CH_2), 48.8 (CH_2), 26.1 (CH_3), 21.4 (CH_3), 18.5 (C), 18.4 (C), –5.0 (CH_3), –5.1 (CH_3); **m.p.** 170 °C; **IR** 2950, 2928, 2855, 1614, 1590, 1475, 1460, 1437, 1385, 1360, 1245, 1085, 833, 775, 732; **UV/VIS** (CH_2Cl_2, 1.10^{-5} M, λ_{max} (log ε)) = 321 (4.24), 287 (4.23), 227 (4.53); **CD** (CH_2Cl_2, 1.10^{-5} M, 20 °C) λ (Δε) 328 (–49.8), 280 (–20.7), 245 (–38.3); $[\alpha]_D^{20}$ = –500 (c = 0.080, CH_2Cl_2).

(+)-(*R*,*P*)-13b-Methanesulfinyl-*p*-tolyl-1,13-dimethoxy-5,9-bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-9,13b-dihydro-5*H*-5,9-diaza-naphtho-[3,2,1-*de*] anthracene: Synthesized (446 mg, 49% yield) using previously reported conditions[1,2] starting from 0.2 mmol of the racemic substrate. This diastereomer corresponds to the least eluted fraction (SiO_2 (20 x 0.5 cm), Et_2O/Pentane (60:40 then 80:20), $\boldsymbol{R_f}$ (Et_2O) = 0.60). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.28 (t, ^3J = 8.3 Hz, 1H), 7.08 (t, ^3J = 8.1 Hz, 1H), 7.04-6.99 (m, 3H), 6.81 (d, ^3J = 8.1 Hz, 2H), 6.76 (d, ^3J = 8.1 Hz, 1H), 6.65 (d, ^3J = 8.3 Hz, 1H), 6.55 (t, ^3J = 8.1 Hz, 2H), 6.49 (d, ^3J = 8.1 Hz, 1H), 6.43 (d, ^3J = 8.3 Hz, 1H), 4.08-3.84 (m, 9H), 3.83 (s, 3H), 3.80-3.72 (m, 1H), 3.34 (s, 3H), 2.31 (s, 3H), 0.93 (s, 9H), 0.92 (s, 9H), 0.93 (s, 9H), 0.92 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 161.5 (C), 157.5 (C), 143.3 (C), 142.8 (C), 142.3 (C), 140.6 (C), 140.3 (C), 140.0 (C), 129.3 (CH), 129.2 (CH), 127.1 (CH), 126.4 (CH), 124.6 (CH), 116.8 (C), 111.5 (C), 110.9 (C), 107.4 (CH), 106.5 (CH), 105.9 (CH), 105.5 (CH), 105.4 (CH), 102.5 (CH), 67.6 (CH_2), 60.1 (CH_2), 59.8 (CH_2), 56.1 (CH_3), 55.4 (CH_3), 49.6 (CH_2), 48.6 (CH_2), 26.1 (CH_3), 26.0 (CH_3), 21.5 (CH_3), 18.5 (C), 18.4 (C), –5.0 (CH_3), –5.1 (CH_3); **m.p.** 158 °C; **IR** 2950, 2928, 2855, 1614, 1590, 1475, 1460, 1385, 1245, 1085, 1037, 833, 775, 732; **UV/VIS** (CH_2Cl_2, λ_{max} (log ε)) = 321 (4.20), 287 (4.21), 227 (4.54); **CD** (CH_2Cl_2, 1.10^{-5} M, 20 °C) λ(Δε) 328 (47.6), 280 (42.1), 250 (45.7), 230 (–64.7); $[\alpha]_D^{20}$= +615 (c = 0.080, CH_2Cl_2).

(–)-(*M*)-**HelOH** or (–)-(*M*)-5,9-bis-(2-hydroxyethyl)-1,13-dimethoxy-5,9-dihydroquinolino[2,3,4-*kl*]acridin-13b-ylium trifluoroacetate salt: Trifluoroacetic anhydride (2.3 mL, 16.2 mmol, 50 equiv.) was added at 25 °C, to a solution of the (*R*,*M*)-sulfoxyde adduct (0.3 mmol) in dichloromethane (5 mL). The initially colorless solution immediately turned blue-green. After 20 min, concentration *in vacuo* followed by several washings with Et_2O afforded the crude product which was further purified over basic alumina (CH_2Cl_2/ MeOH: 97/3) to give the desired enantiopure salt (85% yield). $\boldsymbol{R_f}$ = 0.23 (CH_2Cl_2/MeOH: 97/3); **^{1}H-NMR** (400 MHz, $(CD_3)_2CO$) δ 8.12 (t, ^3J = 8.6 Hz, 1H), 7.91 (t, ^3J = 8.6 Hz, 2H), 7.88 (d, ^3J = 8.6 Hz, 2H), 7.77 (d, ^3J = 8.8 Hz, 2H), 6.99 (d, ^3J = 8.1 Hz, 2H), 5.79-5.29 (s, br, 2H), 5.00-4.92 (m, 2H), 4.81-4.72 (m, 2H), 4.26-4.16 (m, 4H), 3.79 (s, 6H); **^{13}C-NMR** (100 MHz, $(CD_3)_2CO$) δ 160.4 (C), 143.6 (C), 140.1 (C), 137.7 (CH), 137.1 (CH), 120.0 (C), 113.8 (C), 109.2 (CH), 106.8 (CH), 103.6 (CH), 58.9 (CH_2), 56.1 (CH_3), 52.6 (CH_2); **^{19}F NMR** ($(CD_3)_2CO$, 376 MHz) δ –75.4; **IR** 3365, 2933, 2850, 1682, 1607, 1584, 1557, 1503, 1346, 1266, 1254, 1203, 1174, 1133, 815, 762, 722, 632, 544, 535; **CD** (CH_2Cl_2, 1.10^{-5} M, 20°C) λ(Δε) 626 (–2.5), 458 (5.2), 409 (–4.7), 350 (–42.0), 320 (–19.1), 310 (34.8), 284 (–91.0), 243 (–18.0); **CD** (H_2O, 1.10^{-5} M, 20 °C) λ (Δε) 630 (–2.5), 450 (8.0), 350 (–42.7), 320 (–15.0), 310 (36.1), 280 (–91.2), 243 (–12.7); $[\alpha]_{435}^{20}$ = –5200; $[\alpha]_{365}^{20}$ = – 13300 (c = $5.3.10^{-4}$, CH_2Cl_2); $[\alpha]_{435}^{20}$ = – 5700; $[\alpha]_{365}^{20}$ = – 14500 (c = $5.3.10^{-4}$, H_2O); **MS** (ESI^+, m/z) 417.3; **MS** (ESI^-, m/z) 113.4.

(+)-(*P*)-**HelOH** or (+)-(*P*)-5,9-bis-(2-hydroxyethyl)-1,13-dimethoxy-5,9-dihydroquinolino[2,3,4-*kl*]acridin-13b-ylium trifluoroacetate salt: Synthesized using the procedure described above starting from (*R*,*P*)-sulfoxyde adduct. **CD** (CH_2Cl_2, 1.10^{-5} M, 20 °C) l (De) 626 (2.7), 458 (–5.3), 409 (4.8), 350 (42.2), 320 (19.0), 310 (–35.0), 284 (91.4), 243 (18.2); **CD** (H_2O, 1.10^{-5} M, 20 °C) l (De) 630 (2.4), 450 (–8.2), 350 (43.0), 320 (15.2), 310 (–36.2), 280 (91.0), 243 (12.5); $[\alpha]_{435}^{20}$ = + 5100; $[\alpha]_{365}^{20}$ = + 13000 (c = $5.3.10^{-4}$, CH_2Cl_2); $[\alpha]_{435}^{20}$ = + 5500; $[\alpha]_{365}^{20}$ = + 14300 (c = $5.3.10^{-4}$, H_2O).

Spectroscopic Measurements

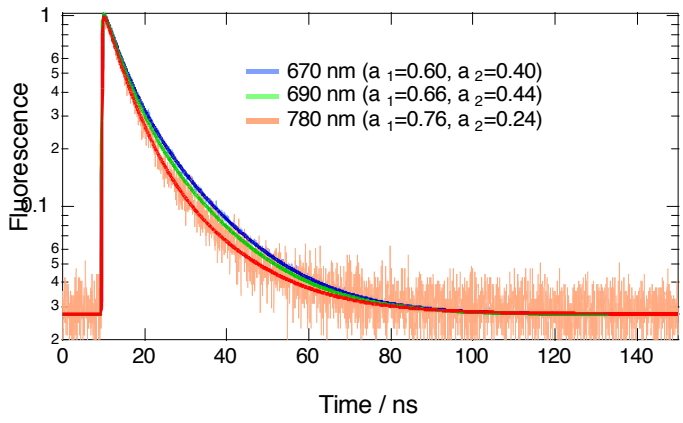

Figure S1. Normalized time profiles of 10^{-5} M solution of *(rac)*-HelPr in chloroform. A1 and A2 are relative amplitudes of the components with the time constants τ_1 = 4.6 ns and τ_2 = 14.8 ns.

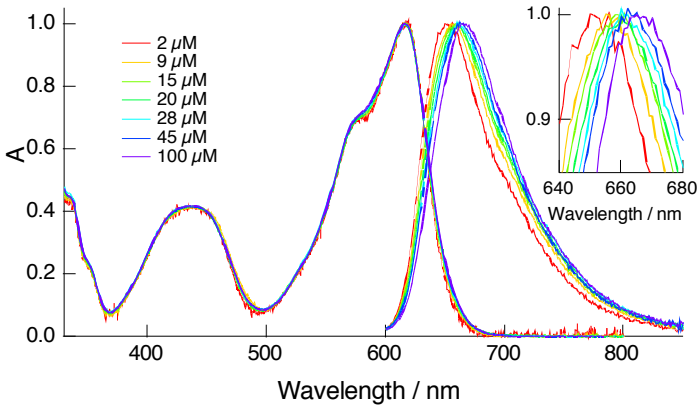

Figure S2. Normalized absorption and emission spectra of various concentrations of *(rac)*-HelPr in chloroform. Inset: same emission spectra in the 640-680 nm region.

Table S1. Time constants and relative amplitudes obtained from the analysis of the fluorescence decay of *(rac)*-HelPr at various concentrations in chloroform.

[(rac)-HelPr]	650 nm		670 nm		690 nm		780 nm	
	τ_1/ns (A_1)	τ_2/ns (A_2)	τ_1/ns (A_1)	τ_2/ns (A_2)	τ_1/ns (A_1)	τ_2/ns (A_2)	τ_1/ns (A_1)	τ_2/ns (A_2)
6.3 μM	4.4 (0.40)	14.9 (0.60)	4.7 (0.55)	15.0 (0.45)	4.7 (0.61)	15.0 (0.39)	5.0 (0.73)	15.8 (0.27)
11 μM	4.5 (0.47)	14.8 (0.53)	4.5 (0.62)	14.8 (0.38)	4.7 (0.68)	14.9 (0.32)	4.9 (0.78)	15.8 (0.22)
18 μM	4.6 (0.56)	14.9 (0.44)	4.6 (0.68)	14.8 (0.32)	4.7 (0.73)	14.9 (0.27)	4.9 (0.82)	15.5 (0.18)
26 μM	4.5 (0.60)	14.7 (0.40)	4.6 (0.71)	14.7 (0.29)	4.7 (0.76)	14.9 (0.24)	4.8 (0.83)	15.2 (0.17)

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(2) Mehanna, N. Ph. D. Thesis, University of Geneva, 2010.