Supporting Information

Hierarchical Helices of Helices Directed by Pt···Pt and π–π Stacking Interactions: Reciprocal Association of Multiple Helices of Dinuclear Alkynylplatinum(II) Complex with Luminescence Enhancement Behavior

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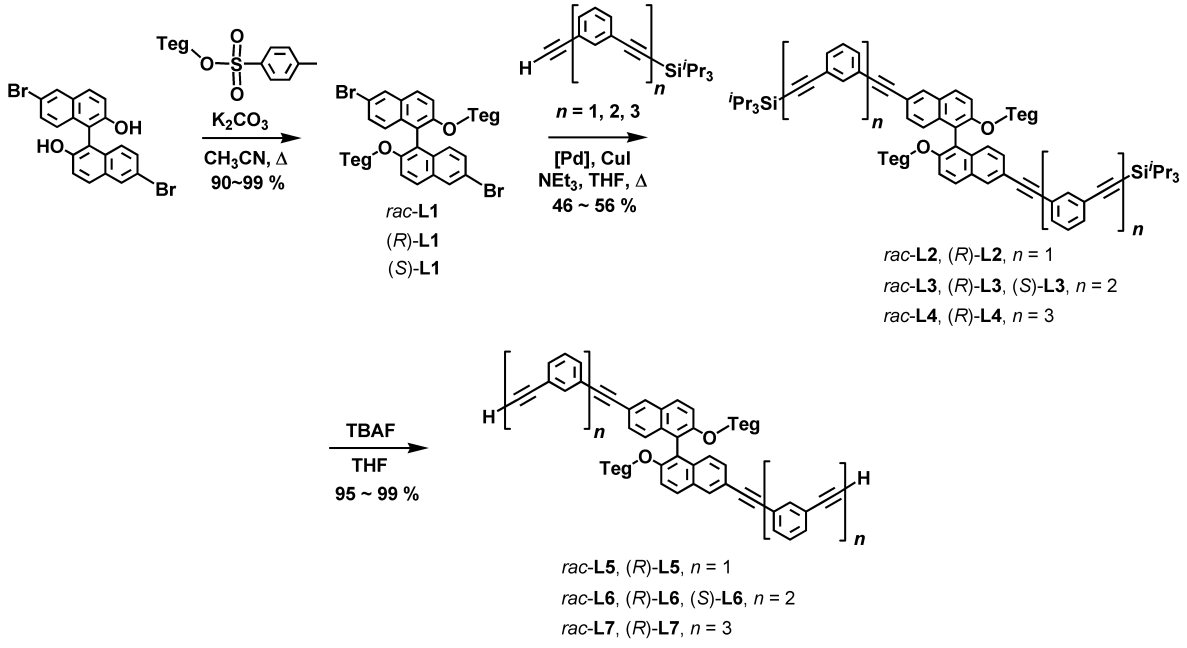
Experimental Section

Materials and Reagents. Dichloro(1,5-cyclooctadiene)platinum(II) (Strem Chemicals Co. Ltd), 3-bromoiodobenzene (Apollo Scientific Ltd.), 1,3-diiodobenzene (Alfa Aesar Chemical Co. Ltd.), tetra-*n*-butylammonium fluoride (Sigma-Aldrich Co. Ltd., 1.0 M), trimethylsilylacetylene (GFS Chemical Co. Ltd.), triisopropylacetylene (GFS Chemical Co. Ltd.) and triethylamine (Apollo Scientific Ltd) were purchased from the corresponding chemical company. 6,6'-Dibromo-bi-2-naphthol derivative, **L1** was synthesized and characterized as described previously.[21a] Dichloromethane (Sigma-Aldrich Co. Ltd., ACS spectrophotometric grade) and acetonitrile (Acros Organics Co. Ltd., spectroscopic grade) were used for spectroscopic studies without further purification.

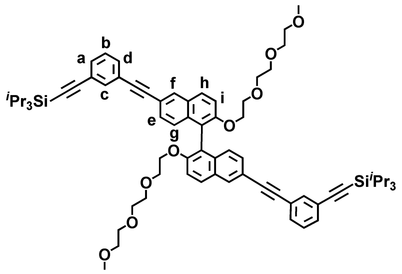
Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 or 500 (400 and 500 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane, $(CH_3)_4Si$. Positive-ion FAB mass spectra were recorded on a Thermo Scientific DFS high resolution magnetic sector mass spectrometer. IR spectra were obtained as KBr disk on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm^{-1}). Elemental analyses of the complexes were performed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. The UV-visible spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. The emission spectra at room temperature were recorded on a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with an R2658P PMT detector. Variable-temperature UV-vis absorption and emission spectra were obtained using a Varian Cary 50 UV-vis spectrophotometer and a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with an R2658P PMT detector, respectively. The temperature was maintained by a Varian Cary single-cell Peltier thermostat. Resonance light-scattering (RLS) experiments were performed on Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer with a Xenon flash lamp using a right-angle geometry to a R2658P PMT detector. Transmission electron microscopy (TEM) experiments were performed on Philips Tecnai G2 20 S-TWIN with an accelerating voltage of 200 kV. The TEM images were taken by Gatan MultiScan model 794. Scanning electron microscopy (SEM) experiments were performed on Hitachi S4800 FEG operating at 4.0-6.0 kV.

Synthesis and Characterization of the Chiral Binaphthol Derivatives

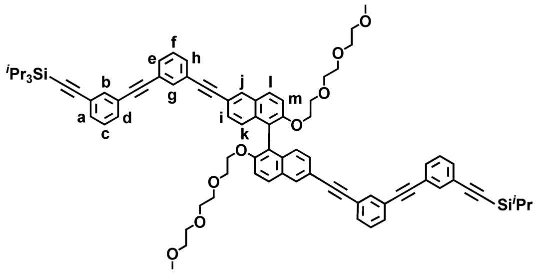
The synthetic route for binaphthol derivatives (*n* = 1, 2 and 3) is shown in Scheme S1.



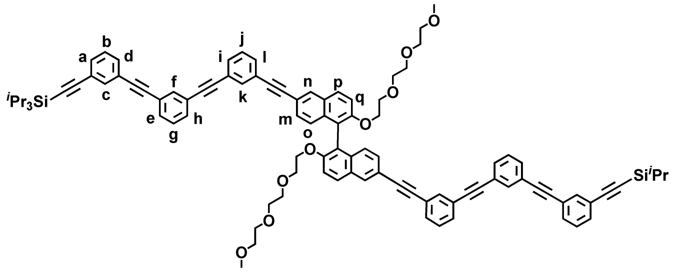
Scheme S1. Synthetic route for binaphthol derivatives (*n* = 1, 2 and 3)



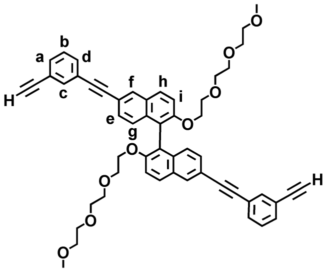
Synthesis of L2: To a 100-ml two-necked round-bottomed flask fitted with a magnetic stirrer were added **L1** (500 mg, 0.7 mmol), tris(dibenzylideneacetone)dipalladium(0) (39 mg, 0.04 mmol) and copper(I) iodide (6 mg, 0.04 mmol). Dry tetrahydrofuran (50 ml) and triethylamine (20 ml) were then transferred to the mixture. 1-Ethynyl-3-triisopropylsilylethynylbenzene (569 mg, 2.1 mmol) was added. The reaction mixture was heated to reflux for 72 h. The resulting mixture was evaporated to dryness and the residue was purified by column chromatography (70-230 mesh) using hexane-ethyl acetate mixture (1:1 v/v) or chloroform-hexane (5:1 v/v) mixture as eluent to give **L2** as a pale yellow oil. Yield: 356 mg (46 %).^{1}H NMR (400 MHz, CDCl$_3$, 300 K, relative to Me$_4$Si): δ = 1.14 (d, 36H, –Si{CH(C*H*$_3$)$_2$}$_3$), 1.26 (m, 6H, –Si{C*H*(CH$_3$)$_2$}$_3$), 3.18 (m, 4H, –TEG), 3.26 (m, 4H, –TEG), 3.33 (s, 6H, –TEG), 3.46 (m, 12H, –TEG), 4.12 (m, 4H, –TEG), 7.10 (d, *J* = 8.8 Hz, 2H, *H$_i$*), 7.29 (t, *J* = 7.4 Hz, 2H, *H$_b$*), 7.30 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H, *H$_h$*), 7.43 (m, 4H, *H$_a$* and *H$_g$*), 7.46 (dt, *J* = 7.9 Hz, *J* = 1.3 Hz, 2H, *H$_d$*), 7.66 (t, 2H, *J* = 1.3 Hz, 2H, *H$_c$*), 7.91 (d, *J* = 9.1 Hz, 2H, *H$_e$*), 8.07 (s, 2H, *H$_f$*); ^{13}C {^{1}H} NMR (125.8 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ = 11.3 (primary *C* on –Si^{i}Pr$_3$ groups), 31.0 (tertiary *C* on –Si^{i}Pr$_3$ groups), 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on –TEG), 88.1, 89.0, 90.9, 91.5 (*C*≡*C*), 116.0, 117.6, 120.0, 123.9, 128.0, 128.4, 128.7, 128.7, 129.4, 129.6, 155.1 (*C* on naphthalene); IR (nujol): 2121 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 1140.7 $[\mathrm{M}]^+$; elemental analyses calcd (%) for $\mathrm{C_{72}H_{90}O_8Si_2{\cdot}CHCl_3}$: C 69.63, H 7.29; found: C 69.47, H 7.43.



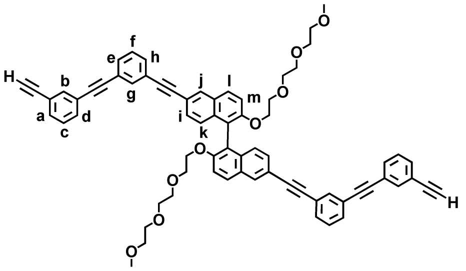
Synthesis of L3: The titled compound was prepared according to the procedure similar to that described for the preparation of **L2**, except *meta*-PE $\mathrm{H\text{-}(C{\equiv}C\text{-}1,3\text{-}C_6H_4)_2\text{-}C{\equiv}C\text{-}Si^{\mathit{i}}Pr_3}$ (779 mg, 2.1 mmol) was used in place of 1-ethynyl-3-triisopropyl-silylethynylbenzene to give **L3** as a pale yellow oil. Yield: 512 mg (56 %). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K, relative to $\mathrm{Me_4Si}$): δ = 1.14 (d, 36H, $-\mathrm{Si\{CH(C}H_3)_2\}_3$), 1.26 (m, 6H, $-\mathrm{Si\{C}H\mathrm{(CH_3)_2\}_3}$), 3.18 (m, 4H, –TEG), 3.26 (m, 4H, –TEG), 3.33 (s, 6H, –TEG), 3.46 (m, 12H, –TEG), 4.12 (m, 4H, –TEG), 7.13 (d, *J* = 8.8 Hz, 2H, H_m), 7.32 (m, 6H, H_c, H_f and H_l), 7.45 (m, 10H, H_a, H_d, H_e, H_h and H_k), 7.66 (t, 2H, *J* = 1.3 Hz, 2H, H_b), 7.73 (t, 2H, *J* = 1.3 Hz, 2H, H_g), 7.92 (d, *J* = 9.1 Hz, 2H, H_i), 8.08 (s, 2H, H_j); ^{13}C {^{1}H} NMR (125.8 MHz, $\mathrm{CDCl_3}$, 298 K, relative to $\mathrm{Me_4Si}$): δ = 11.3 (primary *C* on $-\mathrm{Si^{\mathit{i}}Pr_3}$ groups), 31.0 (tertiary *C* on $-\mathrm{Si^{\mathit{i}}Pr_3}$ groups), 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on –TEG), 88.4, 89.1, 90.9, 91.5 ($C{\equiv}C$), 106.0, 115.9, 118.0, 119.9, 123.2, 123.3, 123.8, 123.9, 125.6, 128.4, 128.5, 128.8, 129.4, 131.2, 131.3, 131.4, 131.7, 131.9, 133.5, 134.6, 135.1, 155.1 (*C* on naphthalene and phenyl rings); IR (nujol): 2124 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 1338.7 $[\mathrm{M}]^+$; elemental analyses calcd (%) for $\mathrm{C_{88}H_{98}O_8Si_2{\cdot}CHCl_3}$: C 73.25, H 6.84; found: C 73.17, H 6.63.



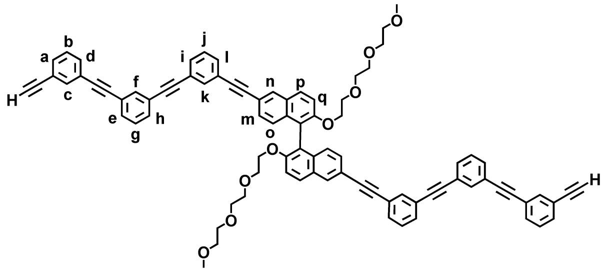
Synthesis of L4: The titled compound was prepared according to the procedure similar to that described for the preparation of **L2**, except *meta*-PE H-(C≡C-1,3-C_6H_4)$_3$-C≡C-Si^{i}Pr$_3$ (989 mg, 2.1 mmol) was used in place of 1-ethynyl-3-triisopropyl-silylethynylbenzene to give **L4** as a pale yellow oil. Yield: 626 mg (50 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 1.14 (d, 36H, $-Si\{CH(CH_3)_2\}_3$), 1.26 (m, 6H, $-Si\{CH(CH_3)_2\}_3$), 3.18 (m, 4H, –TEG), 3.26 (m, 4H, –TEG), 3.33 (s, 6H, –TEG), 3.46 (m, 12H, –TEG), 4.12 (m, 4H, –TEG), 7.12 (d, *J* = 8.8 Hz, 2H, H_q), 7.30 (t, *J* = 7.4 Hz, 2H, H_b), 7.32 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H, H_p), 7.35 (t, *J* = 7.4 Hz, 4H, H_g and H_j), 7.45 (m, 14H, H_a, H_d, H_e, H_h, H_i, H_l and H_o), 7.66 (t, 2H, *J* = 1.3 Hz, 2H, H_c), 7.72 (t, 2H, *J* = 1.3 Hz, 2H, H_f), 7.74 (t, 2H, *J* = 1.3 Hz, 2H, H_k), 7.93 (d, *J* = 9.1 Hz, 2H, H_m), 8.09 (s, 2H, H_n); ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 11.3 (primary *C* on –Si^{i}Pr$_3$ groups), 31.0 (tertiary *C* on –Si^{i}Pr$_3$ groups), 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on –TEG), 88.2, 88.9, 89.0, 89.2, 89.3, 90.9, 91.5 ($C{\equiv}C$), 116.0, 117.6, 120.1, 123.2, 123.3, 123.4, 123.5, 123.9, 124.0, 125.5, 128.3, 128.5, 128.6, 128.7, 129.3, 131.1, 131.3, 131.4, 131.5, 131.7, 131.9, 133.7, 134.6, 134.7, 135.1, 155.4 (*C* on naphthalene and phenyl rings); IR (nujol): 2120 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 1539.4 [M]$^+$; elemental analyses calcd (%) for $C_{104}H_{106}O_8Si_2 \cdot CHCl_3$: C 76.00, H 6.50; found: C 76.17, H 6.43.



Synthesis of L5: To a solution of **L2** (200 mg, 0.2 mmol) in tetrahydrofuran (200 ml) was added a solution of tetra-*n*-butylammonium fluoride (0.1 M) in tetrahydrofuran (1 ml). The solution was stirred for 15 min and the solvent was removed. After that, the residue was purified by column chromatography (70-230 mesh) using chloroform or dichloromethane as eluent to give **L5** as a pale yellow oil. Yield: 141 mg (95 %). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K, relative to Me_4Si): δ = 3.10 (s, 2H, −C≡C*H*), 3.18 (m, 4H, −TEG), 3.26 (m, 4H, −TEG), 3.33 (s, 6H, −TEG), 3.46 (m, 12H, −TEG), 4.12 (m, 4H, −TEG), 7.10 (d, *J* = 8.8 Hz, 2H, H_i), 7.29 (t, *J* = 7.4 Hz, 2H, H_b), 7.30 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H, H_h), 7.43 (m, 4H, H_a and H_g), 7.46 (dt, *J* = 7.9 Hz, *J* = 1.3 Hz, 2H, H_d), 7.66 (t, 2H, *J* = 1.3 Hz, 2H, H_c), 7.91 (d, *J* = 9.1 Hz, 2H, H_e), 8.08 (s, 2H, H_f); ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on −TEG), 82.9, 88.0, 90.9 (*C*≡*C*), 116.0, 117.6, 120.1, 122.6, 124.0, 125.5, 128.4, 128.6, 128.7, 129.3, 131.6, 131.8, 133.7, 135.1, 155.4 (*C* on naphthalene and phenyl rings); IR (nujol): 2122 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 827.5 [M]$^+$; elemental analyses calcd (%) for $C_{54}H_{50}O_8\cdot H_2O$: C 76.76, H 6.20; found: C 76.78, H 6.41.

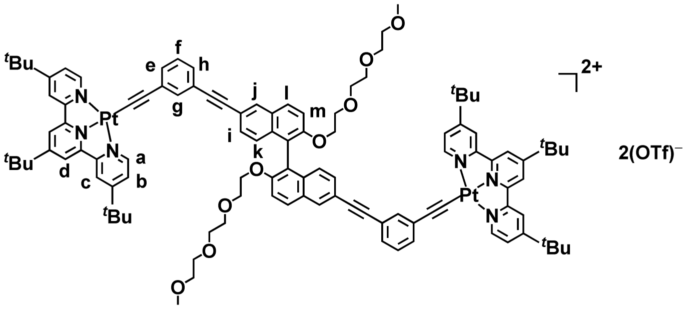


Synthesis of L6: The titled compound was prepared according to the procedure similar to that described for the preparation of **L5**, except **L3** (348 mg, 0.3 mmol) was used in place of **L2** to give **L6** as a pale yellow oil. Yield: 251 mg (99 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ = 3.10 (s, 2H, −C≡C*H*), 3.18 (m, 4H, −TEG), 3.26 (m, 4H, −TEG), 3.33 (s, 6H, −TEG), 3.46 (m, 12H, −TEG), 4.12 (m, 4H, −TEG), 7.12 (d, *J* = 8.8 Hz, 2H, H_m), 7.28 (t, *J* = 7.4 Hz, 2H, H_c), 7.32 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H, H_l), 7.34 (t, *J* = 7.4 Hz, 2H, H_f), 7.45 (m, 10H, H_a, H_d, H_e, H_h and H_k), 7.66 (t, 2H, *J* = 1.3 Hz, 2H, H_b), 7.73 (t, 2H, *J* = 1.3 Hz, 2H, H_g), 7.92 (d, *J* = 9.1 Hz, 2H, H_i), 8.08 (s, 2H, H_j); ^{13}C {^{1}H} NMR (125.8 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ = 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on −TEG), 82.7, 88.4, 88.9, 89.3, 90.6 (*C*≡*C*), 115.9, 117.9, 119.9, 122.5, 123.3, 123.4, 123.8, 125.5, 125.6, 128.4, 128.5, 128.8, 129.5, 131.2, 131.5, 131.7, 131.9, 132.0, 133.5, 134.6, 135.1, 155.2 (*C* on naphthalene and phenyl rings); IR (nujol): 2122 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 1027.3 [M]$^+$; elemental analyses calcd (%) for C$_{70}$H$_{58}$O$_8$·CH$_2$Cl$_2$: C 76.68, H 5.44; found: C 76.57, H 5.51.

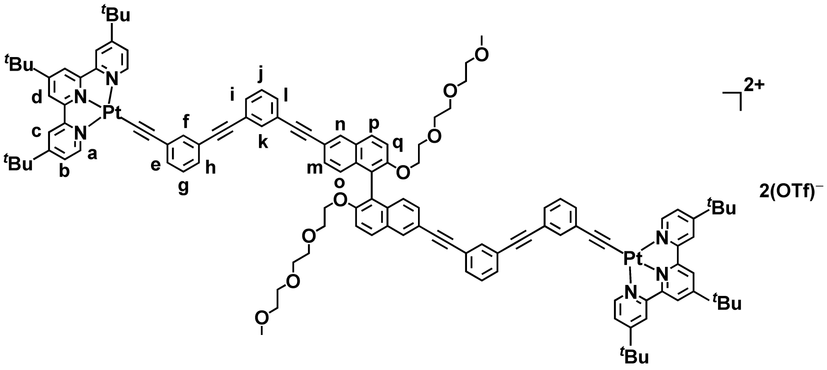


Synthesis of L7: The titled compound was prepared according to the procedure similar to that described for the preparation of **L5**, except **L4** (408 mg, 0.3 mmol) was used in place of **L2** to give **L7** as a pale yellow oil. Yield: 251 mg (99 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ = 3.10 (s, 2H, −C≡C*H*), 3.18 (m, 4H, −TEG), 3.26 (m, 4H, −TEG), 3.33 (s, 6H, −TEG), 3.46 (m, 12H, −TEG), 4.12 (m, 4H, −TEG), 7.12 (d, *J* = 8.8 Hz, 2H, H_q), 7.30 (t, *J* = 7.4 Hz, 2H, H_b), 7.32 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H, H_p), 7.35 (t, *J* = 7.4 Hz, 4H, H_f and H_j), 7.45 (m, 12H, H_a, H_d, H_e, H_h, H_i and H_o), 7.51 (dt, *J* = 7.9 Hz, *J* = 1.3 Hz, 2H, H_l), 7.66 (t, 2H, *J* = 1.3 Hz, 2H, H_c), 7.72 (t, 2H, *J* = 1.3 Hz, 2H, H_f), 7.74 (t, 2H, *J* = 1.3 Hz, 2H, H_k), 7.93 (d, *J* = 9.1 Hz, 2H, H_m), 8.09 (s, 2H, H_n); ^{13}C {^{1}H} NMR (125.8 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ = 60.4, 69.5, 69.6, 70.3, 70.4 (C on –TEG), 82.7, 88.2, 88.9, 89.0, 89.2, 89.3, 90.9 ($C{\equiv}C$), 116.0, 117.6, 120.1, 123.2, 123.3, 123.4, 123.5, 123.9, 124.0, 125.5, 128.3, 128.5, 128.6, 128.7, 129.3, 131.1, 131.3, 131.4, 131.5, 131.7, 131.9, 133.7, 134.6, 134.7, 135.1, 155.4 (C on naphthalene and phenyl rings); IR (nujol): 2120 cm^{-1} ν(C≡C); ESI-MS: ion clusters at m/z 1227.8 $[\mathrm{M}]^{+}$; elemental analyses calcd (%) for $C_{86}H_{66}O_8{\cdot}CHCl_3$: C 77.58, H 5.01; found: C 77.51, H 5.02.

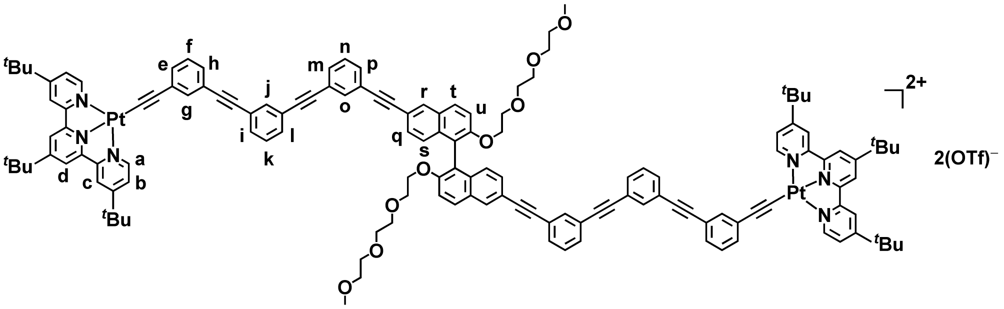
Synthesis and Characterization of the Alkynylplatinum(II) Terpyridine Complexes with the Chiral Binaphthol Derivatives



Synthesis of 1: To a solution of **L5** (30 mg, 0.05 mmol) and $[(^t\mathrm{Bu}_3\mathrm{tpy})\mathrm{PtCl}](\mathrm{OTf})$ (78 mg, 0.10 mmol) in degassed *N*,*N*-dimethylformamide (30 ml) containing triethylamine (5 ml) was added a catalytic amount of CuI. The solution was stirred overnight at room temperature. After removing the solvent, the reaction mixture was purified by chromatography on silica gel using chloroform–acetone mixture (10:1 v/v) as eluent, followed by the diffusion of diethyl ether vapor into an acetonitirile solution of the complex to give **1** as a yellow solid. Yield: 73 mg (68 %).^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 1.40 (s, 18H, –^{t}Bu), 1.57 (s, 9H, –^{t}Bu), 3.18, 3.26, 3.33, 3.46, 4.12 (m, 30H, –TEG), 7.10 (d, J = 8.8 Hz, H_m), 7.31 (m, 4H, H_f and H_l), 7.43 (m, 6H, H_e, H_h and H_k), 7.62 (dd, J = 6.0 Hz, J = 1.6, 4H, H_b), 7.70 (t, J = 1.3 Hz, 2H, H_g), 7.93 (d, J = 9.1 Hz, 2H, H_i), 8.09 (s, 2H, H_j), 8.38 (d, J = 1.6 Hz, 4H, H_c), 8.45 (s, 4H, H_d), 9.15 (d with Pt satellites, J = 6.0 Hz, 4H, H_a); ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 30.5, 30.2 (primary C on –^{t}Bu), 38.8, 37.5 (quaternary C on –^{t}Bu), 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (C on –TEG), 90.4, 88.8 ($C{\equiv}C$), 98.2 (Pt–$C{\equiv}C$), 103.8 (Pt–$C{\equiv}$C), 123.1, 123.5, 126.8 (tertiary C on terpyridyl), 116.0, 117.8, 120.1, 121.7, 125.4, 125.5, 128.3, 128.6, 128.7, 129.2, 129.7, 131.5, 131.6, 133.7, 135.1, 153.9 (C on naphthalene and phenyl ring), 154.0 (tertiary C on terpyridyl), 155.5, 158.8, 167.5, 168.7 (quaternary C on terpyridyl); IR (nujol): 2121 cm^{-1} ν(C≡C); ESI-MS: ion clusters at m/z 1009.1 [M−2OTf]$^{2+}$; elemental analyses calcd (%) for $C_{110}H_{118}F_6N_6O_{14}Pt_2S_2\cdot4CHCl_3$: C 49.00, H 4.40, N 3.01; found: C 49.17, H 4.43, N 3.03.



Synthesis of 2: The titled complex was prepared according to the procedure similar to that described for the preparation of **1**, except **L6** (42 mg, 0.05 mmol) was used in place of **L5**. Yield: 65 mg (73 %).^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 1.40 (s, 18H, –^{t}Bu), 1.57 (s, 9H, –^{t}Bu), 3.18, 3.26, 3.33, 3.46, 4.12 (m, 30H, –TEG), 7.10 (d, J = 8.8 Hz, H_q), 7.31 (m, 6H, H_f, H_j and H_p), 7.49 (m, 10H, H_e, H_g, H_i, H_l and H_o), 7.62 (dd, J = 6.0 Hz, J = 1.6, 4H, H_b), 7.68 (t, J = 1.3 Hz, 2H, H_k), 7.74 (t, J = 1.3 Hz, 2H, H_h), 7.93 (d, J = 9.1 Hz, 2H, H_m), 8.09 (s, 2H, H_n), 8.38 (d, J = 1.6 Hz, 4H, H_c), 8.45 (s, 4H, H_d), 9.15 (d with Pt satellites, J = 6.0 Hz, 4H, H_a); ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 30.5, 30.2 (primary *C* on –^{t}Bu), 38.8, 37.5 (quaternary *C* on –^{t}Bu), 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on –TEG), 88.2, 88.8, 89.7, 90.9 (*C*≡*C*), 98.6 (Pt–C≡*C*), 103.6 (Pt–*C*≡C), 123.1, 123.5, 126.8 (tertiary *C* on terpyridyl), 116.0, 117.6, 120.0, 121.7, 123.0, 123.1, 123.5, 124.0, 125.4, 125.5, 128.4, 128.6, 128.7, 129.2, 129.7, 131.1, 131.4, 131.9, 133.7, 134.6, 135.0, 153.9 (*C* on naphthalene and phenyl ring), 154.0 (tertiary *C* on terpyridyl), 155.5, 158.8, 167.5, 168.7 (quaternary *C* on terpyridyl); IR (nujol): 2123 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 1109.5 [M－2OTf]$^{2+}$; elemental analyses calcd (%) for $C_{129}H_{134}F_6N_6O_{14}Pt_2S_2{\cdot}2CH_2Cl_2$: C 57.62, H 5.09, N 3.07; found: C 57.72, H 4.90, N 3.22.



Synthesis of 3: The titled complex was prepared according to the procedure similar to that described for the preparation of **1**, except **L7** (52 mg, 0.05 mmol) was used in place of **L5**. Yield: 80 mg (70 %).^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 1.40 (s, 18H, –^{t}Bu), 1.57 (s, 9H, –^{t}Bu), 3.18, 3.26, 3.33, 3.46, 4.12 (m, 30H, –TEG), 7.10 (d, *J* = 8.8 Hz, H_u), 7.40 (m, 8H, H_f, H_j, H_n and H_t), 7.48 (m, 14H, H_e, H_h, H_i, H_l, H_m, H_p and H_s), 7.62 (dd, *J* = 6.0 Hz, *J* = 1.6, 4H, H_b), 7.70 (m, 4H, H_k and H_o), 7.72 (t, *J* = 1.3 Hz, 2H, H_g), 7.93 (d, *J* = 9.1 Hz, 2H, H_q), 8.09 (s, 2H, H_r), 8.38 (d, *J* = 1.6 Hz, 4H, H_c), 8.45 (s, 4H, H_d), 9.15 (d with Pt satellites, *J* = 6.0 Hz, 4H, H_a); ^{13}C {^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 30.5, 30.2 (primary *C* on –^{t}Bu), 38.8, 37.5

(quaternary *C* on –^{t}Bu), 60.4, 69.5, 69.6, 70.3, 70.4, 70.6, 71.8 (*C* on –TEG), 88.2, 88.8, 89.7, 90.9 (*C*≡*C*), 98.6 (Pt–C≡*C*), 103.6 (Pt–*C*≡C), 123.1, 123.5, 126.8 (tertiary *C* on terpyridyl), 116.0, 117.6, 120.0, 121.7, 123.0, 123.1, 123.5, 124.0, 125.4, 125.5, 128.4, 128.6, 128.7, 129.2, 129.7, 131.1, 131.4, 131.9, 133.7, 134.6, 135.0, 153.9 (*C* on naphthalene and phenyl ring), 154.0 (tertiary *C* on terpyridyl), 168.7, 167.5, 158.8, 155.5 (quaternary *C* on terpyridyl); IR (nujol): 2122 cm^{-1} ν(C≡C); ESI-MS: ion clusters at *m*/*z* 1209.3 [M−2OTf]$^{2+}$; elemental analyses calcd (%) for $C_{142}H_{134}F_6N_6O_{14}Pt_2S_2 \cdot 3CHCl_3$: C 56.64, H 4.49, N 2.73; found: C 56.40, H 4.41, N 2.80.

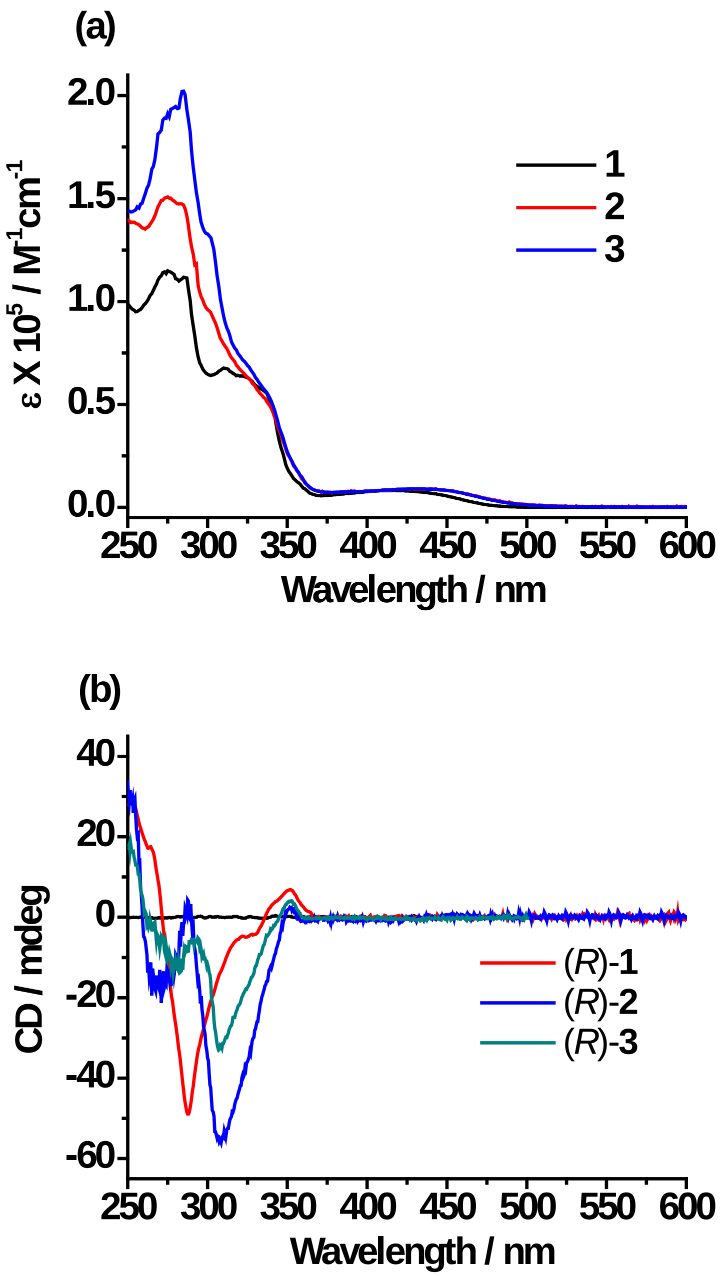


Figure S1. (a) UV-vis absorption spectra and (b) CD spectra of complexes **1**–**3** in acetonitrile.

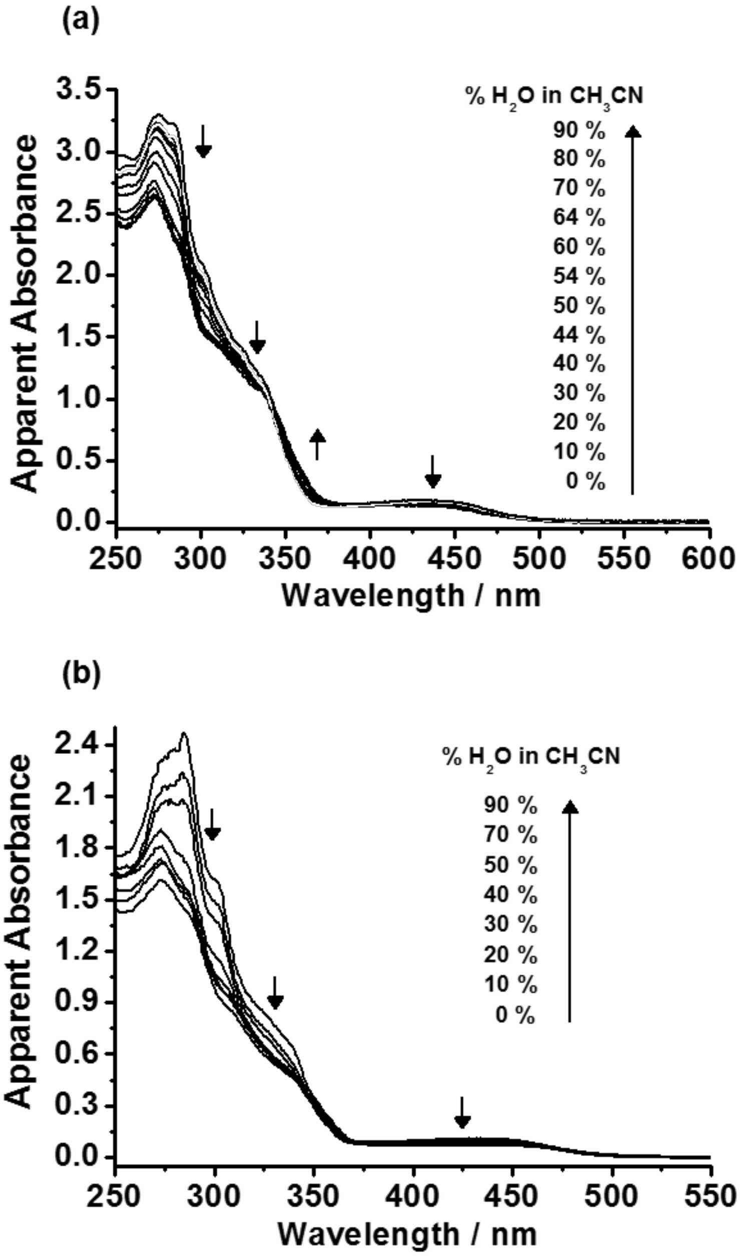


Figure S2. UV-vis absorption spectral traces of (a) *rac*-**2** (1.7×10^{-5} M) and (b) *rac*-**3** (1.3×10^{-5} M) with increasing H_2O content in CH_3CN at 298 K. The apparent absorbance values have been obtained by correcting to a 1-cm path length equivalence.

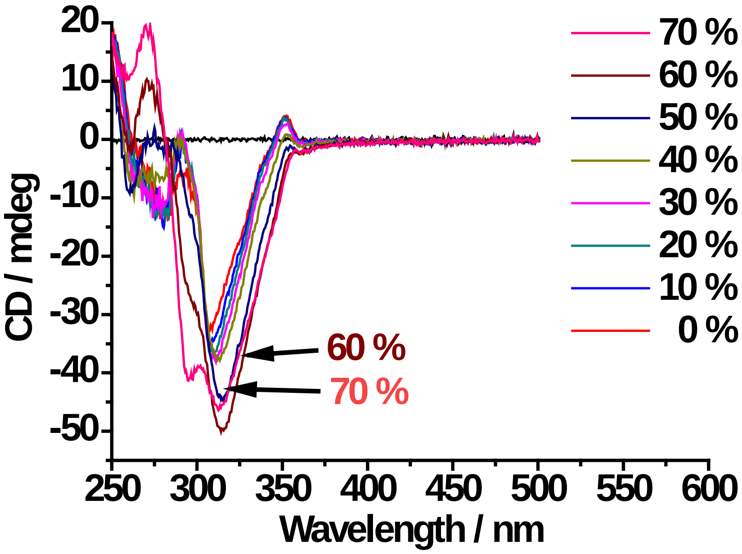


Figure S3. CD spectral traces of (*R*)-**3** in CH_3CN (1.3×10^{-5} M) with increasing H_2O content from 0 to 70 % at 298 K.

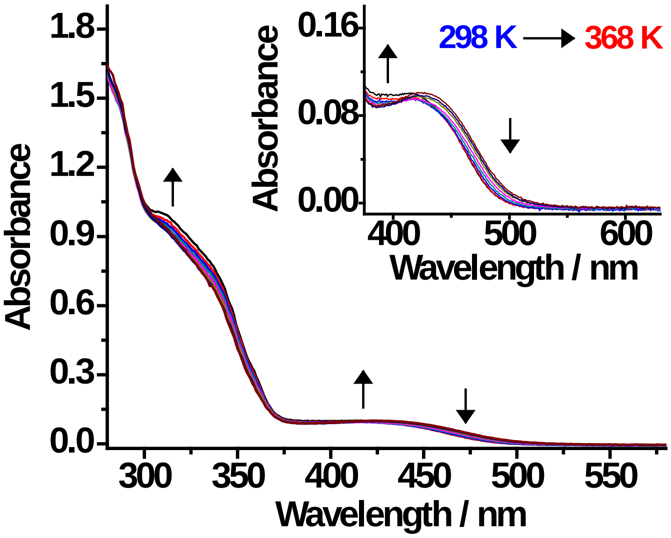


Figure S4. UV-vis spectral traces of (*rac*)-**2** in 70 % H_2O in CH_3CN with increasing temperature.

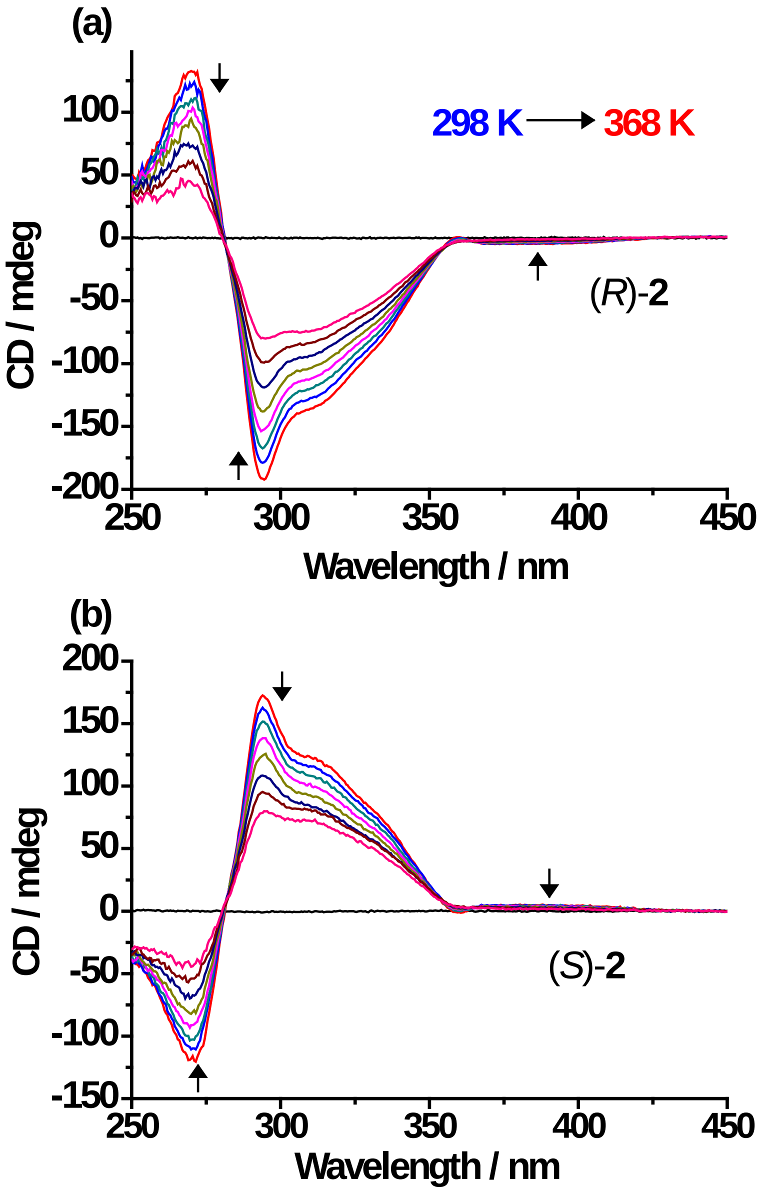


Figure S5. (a) CD spectral traces of (*R*)-**2** and (b) (*S*)-**2** in 70 % H_2O in CH_3CN with increasing temperature.

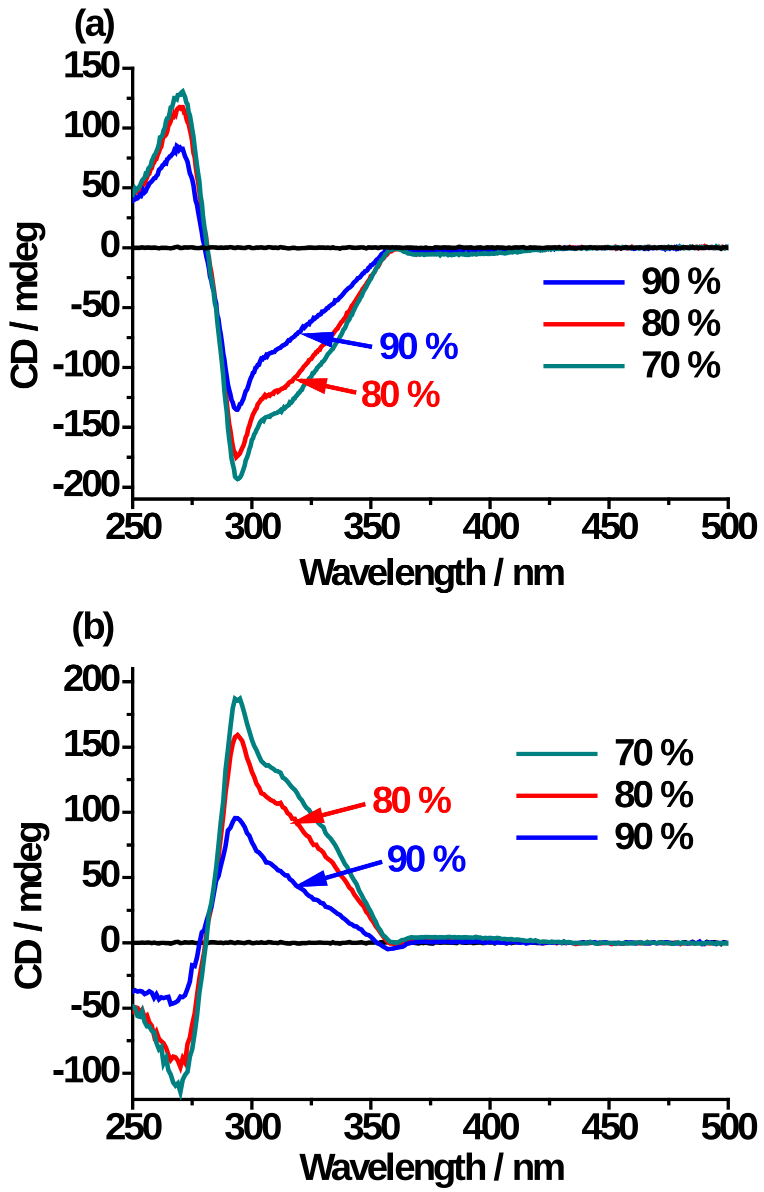


Figure S6. CD spectral traces of (a) (*R*)-**2** (1.7×10^{-5} M) and (b) (*S*)-**2** (1.7×10^{-5} M) in CH_3CN with increasing H_2O content after 70 % at 298 K.

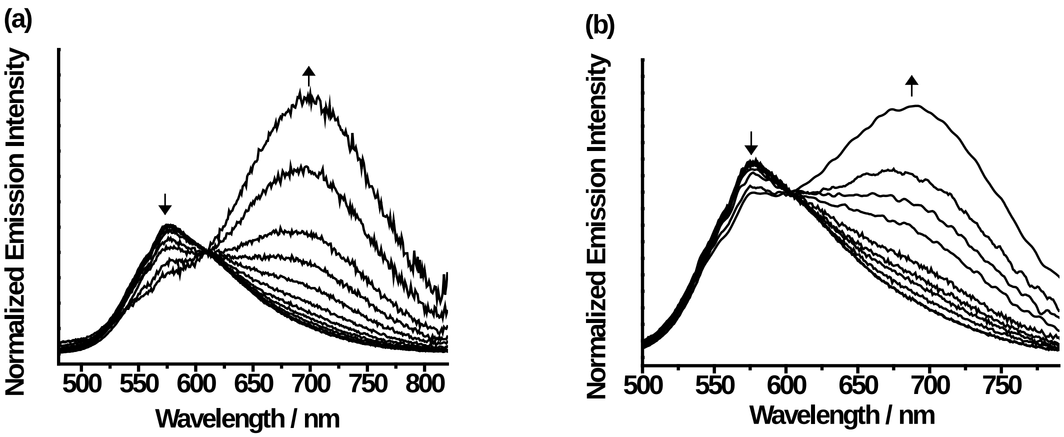


Figure S7. Normalized emission spectral traces of (a) *rac*-**2** at 616 nm and (b) *rac*-**3** at 606 nm upon increasing the CH_3CN content in CH_2Cl_2.

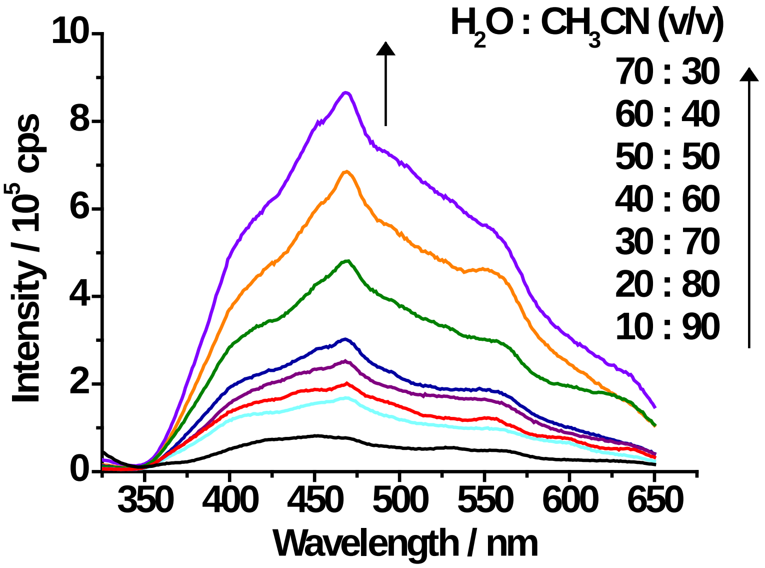


Figure S8. Resonance light scattering (RLS) spectra of (*rac*)-**2** in water–acetonitrile mixture with increasing water content.