Electronic Supporting Information for

Sign Dependence of MCPL spectra on Type and Position of Substituent Group of Pyrene and Phenanthrene Derivatives

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1. Experimental section

1.1 Materials.

1-Methoxypyrene, 1-pyrenecarboxylic acid, 1,2-diethoxyethane, and potassium tert-butoxide were purchased from Tokyo Chemical Industry Co., Ltd. 3-phenanthrenecarboxylic acid was purchased form Sigma-Aldrich and 3-hydroxyphenanthrene was synthesised form 3-methoxyphenanthrene. 3-Methoxyphenanthrene itself was synthesised from same method described for 2-methoxypyrene. Chloroform was purchased from Dojindo (Kumamoto, Japan). 2-Pyrenecarboxylic acid was prepared according to a previously reported method.[S1]

1.2 Instrumentations.

1.2.1 MCPL and PL measurement

The PL and MCPL spectra of the luminophores were acquired using a JASCO CPL-300 spectrofluoropolarimeter equipped with a JASCO PM-491 compact permanent magnet (1.60 T) at room temperature at a scattering angle of 0° upon excitation by unpolarised monochromatic incident light of 10 nm bandwidth. The excitation wavelength for solutions of the pyrene derivatives in $CHCl_3$ was 330 nm, while that for solutions of the phenanthrene derivatives was 270 nm. A 5-mm path length was used for the solution-state spectroscopy measurements.

1.2.2 NMR spectra

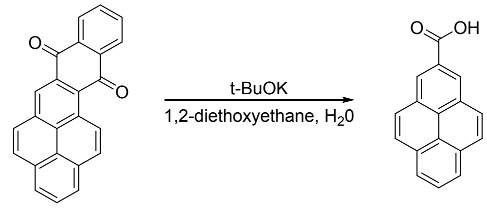
The ^1H and ^{13}C NMR spectra were recorded using JEOL ECA 600, JEOL 400, and JEOL 300 spectrometers. Tetramethylsilane (Me_4Si) was used as an internal reference.

1.2.3 Mass spectra

Mass spectra were recorded using an LCMS-IT-TOF mass spectrometer (Shimadzu Co.) under the following conditions: ionisation method, electrospray ionisation; mass range, m/z 50–2000; mode, positive mode. Calibration and machine tuning was performed using a sodium trifluoroacetate standard solution in acetonitrile for LCMS-IT-TOF (Shimadzu GLC Co.).

1.2.4 Synthesis of 2-pyrenecarboxylic acid (2c) [S1]

The ^1H and ^{13}C NMR spectra were recorded using JEOL ECA 600, JEOL 400, and JEOL 300 spectrometers. Tetramethylsilane (Me_4Si) was used as an internal reference.



2c

Scheme S1. Synthetic route to 2-pyrenecarboxylic acid.

A mixture of the precursor (330 mg, 1.0 mmol) in 1,2-diethoxtethane (7 mL), H_2O (50 µL, 3.0 mmol) and potassium tert-butoxide (1.12 g, 10 mmol) was heated under reflux for 7 h. After cooling to room temperature and removing the solvent, the residue was cooled to 0 °C and conc. HCl was added to give a pH of 1. The residue was then filtered and stirred overnight in H_2O (50 mL). After this time, the mixture was filtered, washed with H_2O (5 mL), and the residue was purified by silica gel column chromatography using CH_2Cl_2/hexane (1:1, v/v) and CH_2Cl_2/MeOH (10:1, v/v) as the eluents to obtain 2-PyCOOH (2c) (22.8 mg, 9% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.87 (s, 2H), 8.36 (d, *J* = 7.8 Hz, 2H), 8.32 (d, *J* = 9.2 Hz, 2H), 8.26 (d, *J* = 9.2 Hz, 2H), 8.16 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 168.4, 131.8, 131.1, 128.8, 128.6, 128.3, 127.8, 126.4, 126.1(2C), 123.9; MS: found *m/z* 245.0593, Calcd. *m/z* 245.0608 for [M]– (M: $C_{17}H_{10}O_2$).

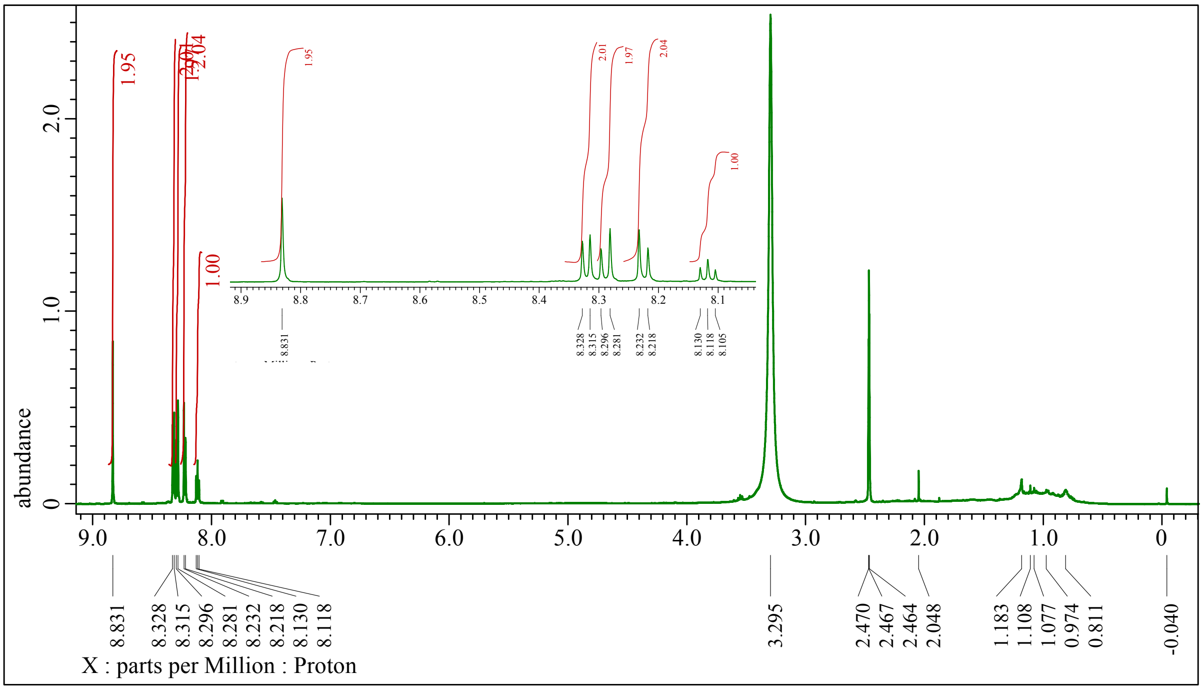


Fig. S1. ^{1}H NMR spectrum of 2-PyCOOH (600 MHz, $CDCl_3$, 298 K, Me_4Si).

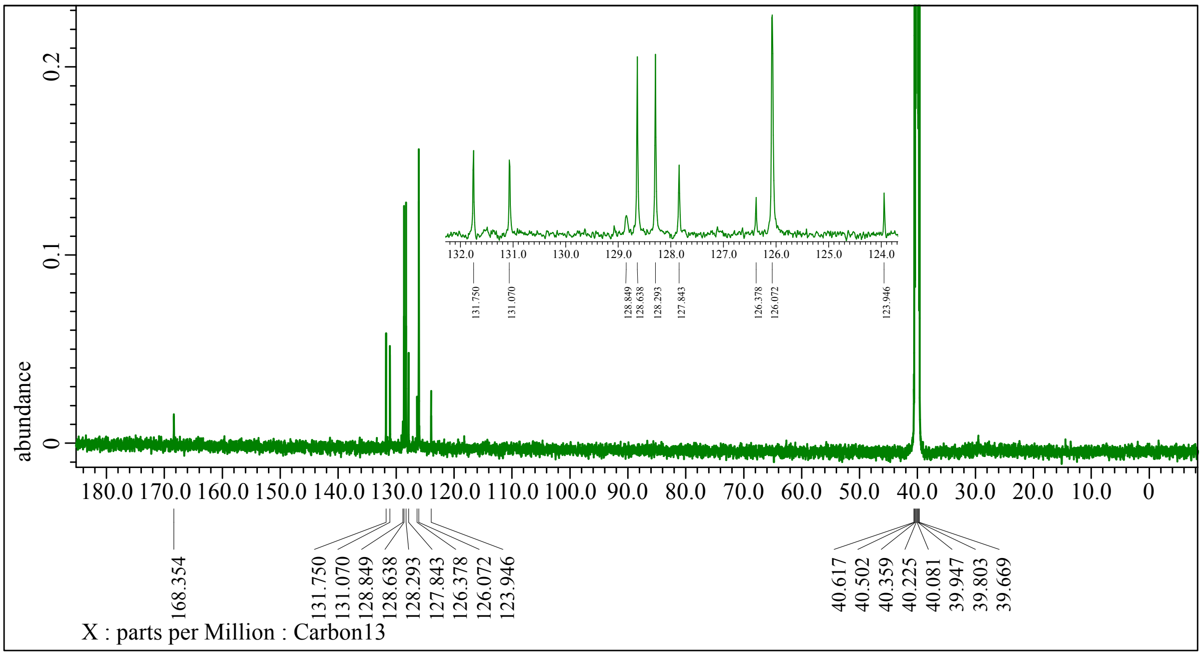


Fig. S2. ^{13}C NMR spectrum of 2-PyCOOH (150 MHz, $CDCl_3$, 298 K, Me_4Si).

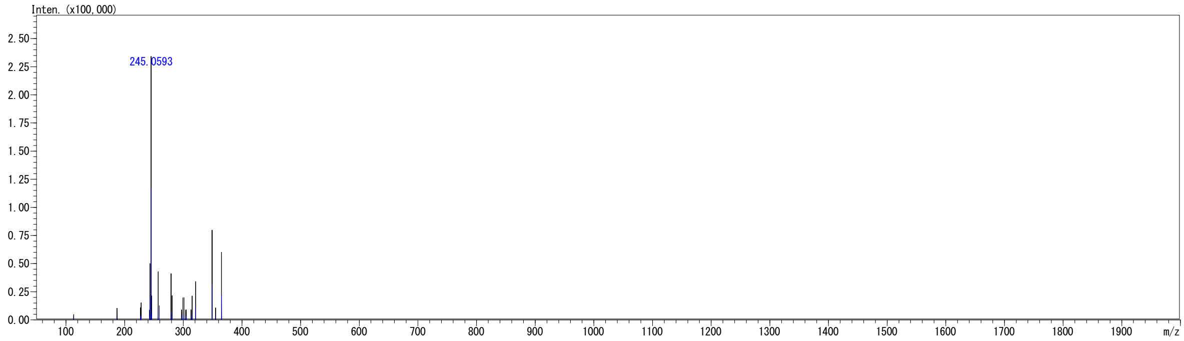
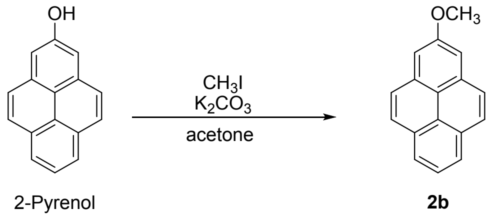


Fig. S3. Mass spectrum of 2-PyCOOH..

1.2.5 Synthesis of 2-methoxypyrene (2b) ^{S2}



Scheme S2. Synthetic route to 2-methoxypyrene.

A mixture of 2-pyrenol (300 mg, 1.37 mmol, 1 equiv), iodomethane (293 mg, 2.06 mmol, 1.5 equiv), and K_2CO_3 (228 mg, 1.65 mmol, 1.2 equiv) in acetone (10 mL) was heated under reflux for 18 h. After evaporation of the acetone, the residue was purified by column chromatography (silica, hexane/ethyl acetate, 6:1) to afford the product as a pale yellow solid (210 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 8.13 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.91 (t, *J* = 7.6 Hz, 1H), 7.70 (s, 2H), 4.07 (s, 1H, OCH_3). ^{13}C NMR (100 MHz, .$CDCl_3$, TMS): δ (ppm) = 157.8, 132.6, 130.1, 128.0, 126.8, 125.2, 124.9, 124.6, 120.0, 110.3, 55.7.

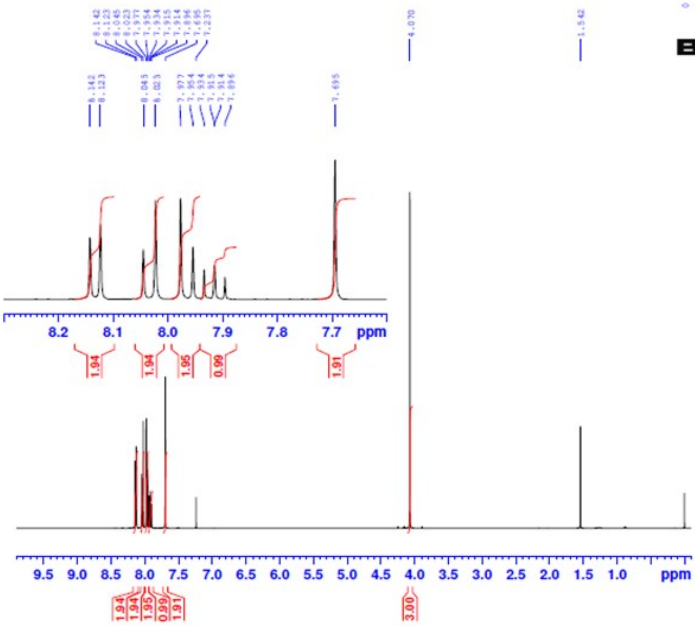


Fig. S4. ^{1}H NMR spectrum of 2-$PyOCH_3$ (400 MHz, $CDCl_3$, 298 K, Me_4Si).

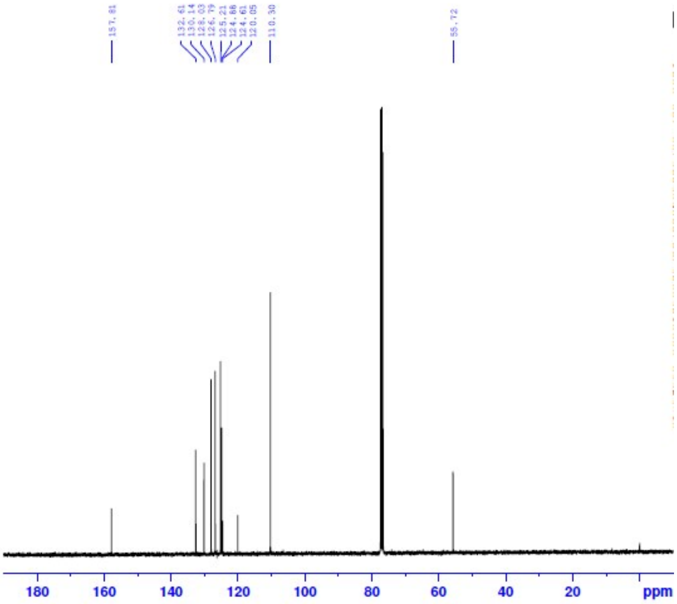
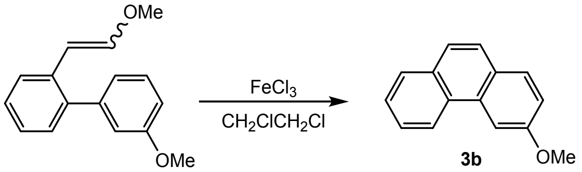


Fig. S5. ^{13}C NMR spectrum of 2-$PyOCH_3$ (100 MHz, $CDCl_3$, 298 K, Me_4Si).

1.2.6. Synthesis of 3-methoxyphenanthrene (3b)



Scheme S3. Synthetic route to 3-methoxyphenanthrene.

A mixture of 3'-methoxy-2- (2-methoxyvinyl)-1,1'-biphenylS2 (2.46 g, 10.2 mmol, 1 equiv), and FeCl$_3$ (98 mg, 0.60 mmol, 0.05 equiv) in dichloroethane (32 mL) was stirred at room temperature for 2 h. After this time, the solvent was removed in vacuo and the residue was subjected to column chromatography (silica, hexane/chloroform, 4:1) to provide the product as a white solid (R_f = 0.18, 1.68 g, 79 %). ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ (ppm) = 8.59 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 2.4 Hz, 1H), 7.86 (dd, J = 1.9, 7.2 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.70-7.54 (m, 4H), 7.24 (dd, J = 2.5, 8.7 Hz, 1H, overlapped with CHCl$_3$), 4.01 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ (ppm) = 158.4, 132.4, 131.6, 129.9, 129.7, 128.6, 126.7, 126.6, 126.5 126.1 124.5 122.6 116.7, 104.0, 55.4.

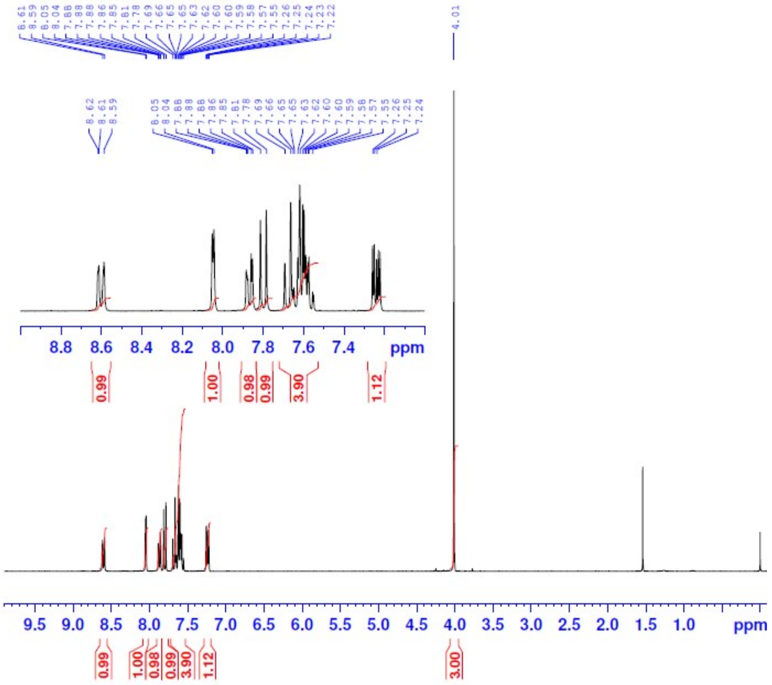


Fig. S6. ^{1}H NMR spectrum of **3-PheOCH$_3$** (300 MHz, CDCl$_3$, Me$_4$Si).

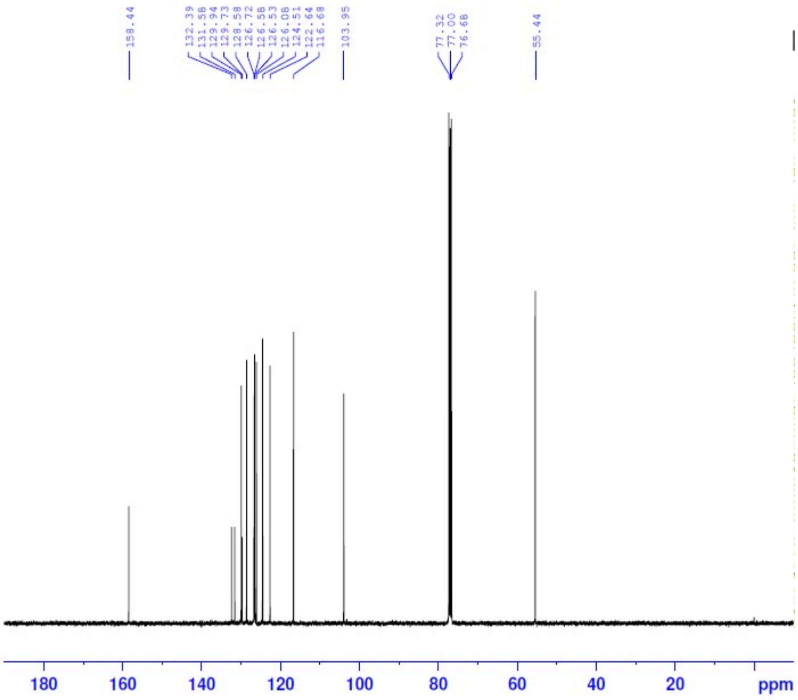
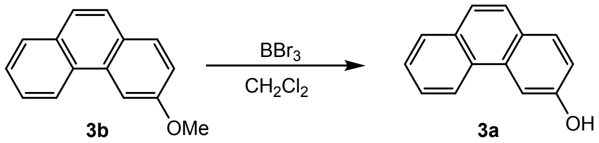


Fig. S7. ^{13}C NMR spectrum of **3-PheOCH$_3$** (100 MHz, CDCl$_3$, Me$_4$Si).

1.2.7. Synthesis of 3-hydrothoxyphenanthrene



Scheme S4. Synthetic route to 3-hydroxyphenanthrene.

Boron tribromide (25 mL, 25.0 mmol, 1.3 equiv) was added to a solution of 3-methoxyphenanthrene (4.0 g, 19.2 mmol) in dichloromethane (223 mL) at 0 °C, and then stirred for 18 h at room temperature. After this time, a standard aqueous workup with chloroform was carried out. After extraction, the combined organic layers were washed with water and then dried over anhydrous Na$_2$SO$_4$. Following concentration in vacuo, the residue was subjected to column chromatography (silica, hexane/ethyl acetate, 5:1) to provide the product as a pale purple solid (R_f = 0.27, 3.64 g, 97%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) = 8.50–8.43 (m, 1H), 7.99 (d, J = 2.3 Hz, 1H), 7.87–7.81 (m, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.60–7.52 (m, 3H), 7.14 (dd, J = 2.4, 8.6 Hz, 1H), 5.28 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ (ppm) = 154.2, 132.4, 131.8, 130.3, 129.5, 128.5, 126.8, 126.7, 126.5 126.2 124.6 122.7 116.6, 106.9.

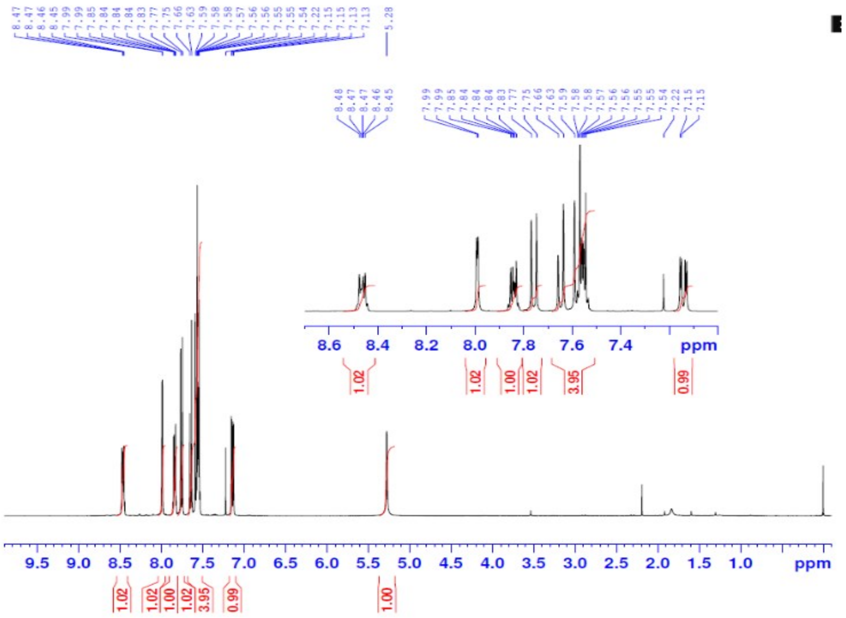


Fig. S8. ^{1}H NMR spectrum of 3-PheOH (400 MHz, $CDCl_3$, 298 K, Me_4Si).

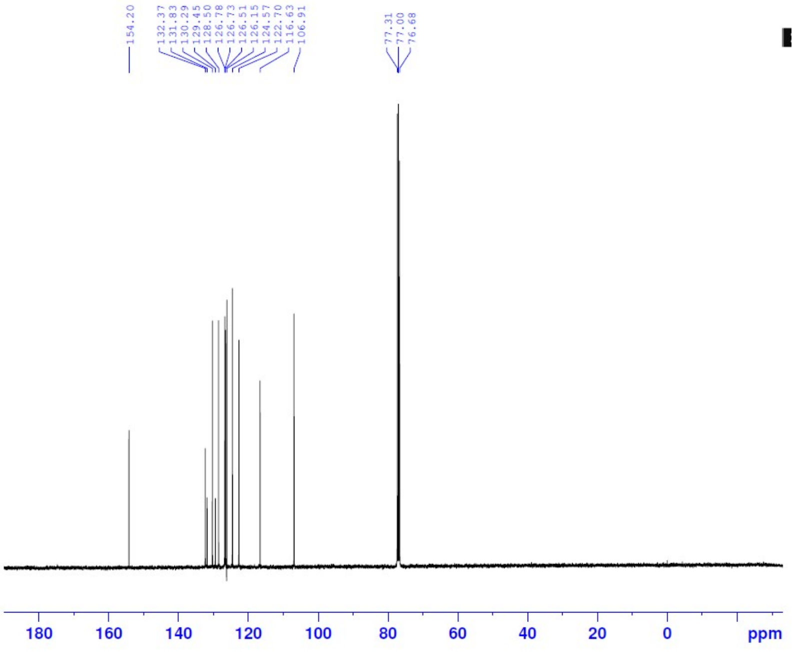


Fig. S9. ^{13}C NMR spectrum of 3-PheOH (400 MHz, $CDCl_3$, 298 K, Me_4Si).

2. MCPL and PL spectra of 1-methoxypyrene (1b; 1-PyOCH$_3$) in CHCl$_3$ under an external magnetic field of 1.6 T

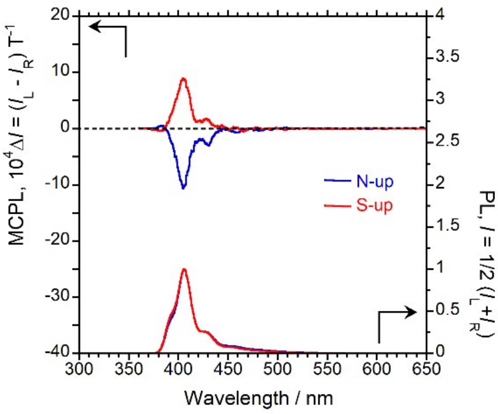


Fig. S10. MCPL and PL spectra of 1-PyOCH$_3$ in CHCl$_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

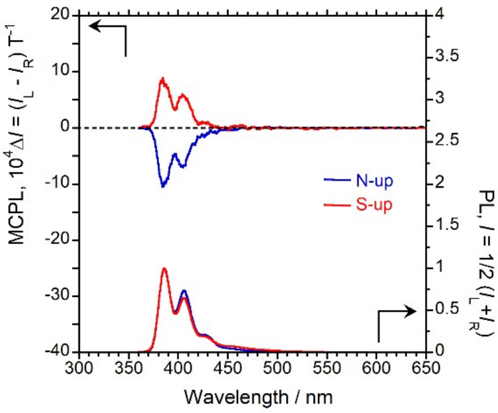


Fig. S11. MCPL and PL spectra of 1-PyOCH$_3$ in CHCl$_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

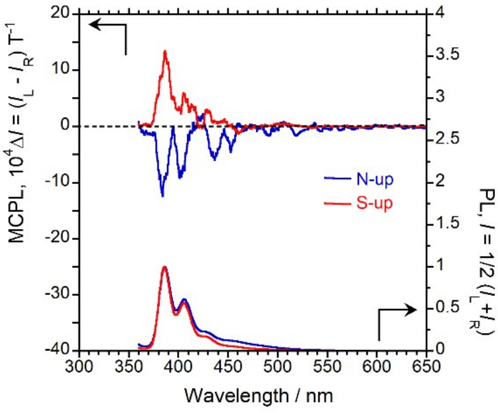


Fig. S12. MCPL and PL spectra of 1-PyOCH$_3$ in CHCl$_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

3. MCPL and PL spectra of 1-pyrenecarboxylic acid (1c; 1-PyCOOH) in $CHCl_3$ under an external magnetic field of 1.6 T

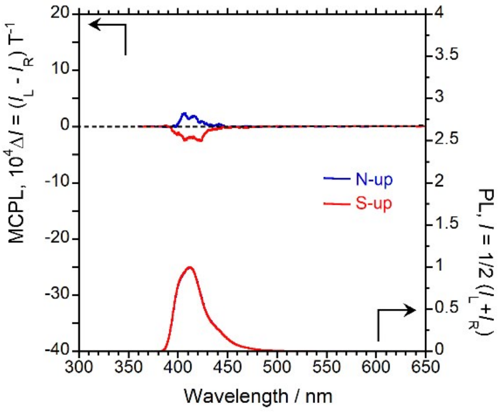


Fig. S13. MCPL and PL spectra of 1-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

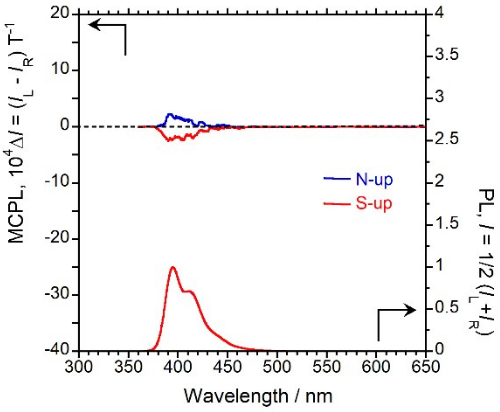


Fig. S14. MCPL and PL spectra of 1-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

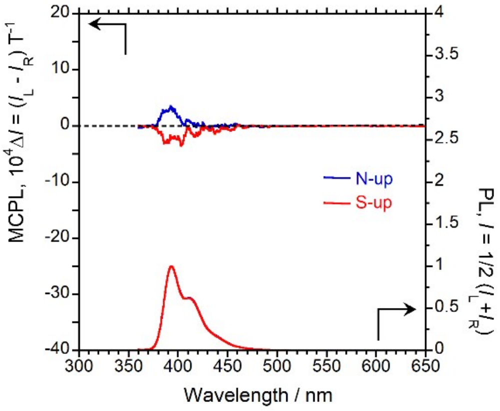


Fig. S15. MCPL and PL spectra of 1-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

4. MCPL and PL spectra of 2-hydroxypyrene (2a; 2-PyOH) in $CHCl_3$ under an external magnetic field of 1.6 T

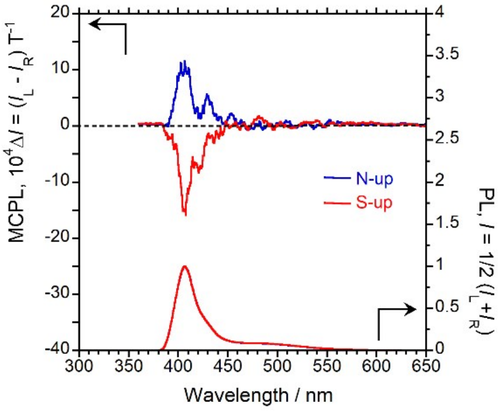


Fig. S16. MCPL and PL spectra of 2-hydroxypyrene in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-2} M, path length = 5 mm, 25 °C).

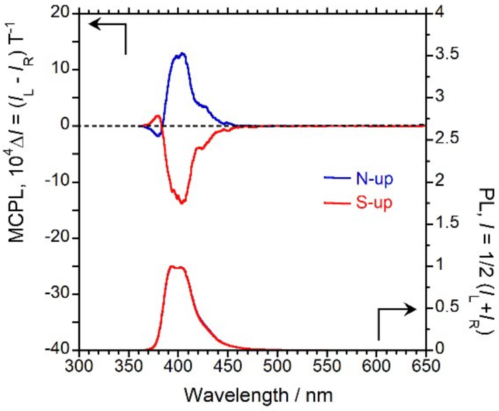


Fig. S17. MCPL and PL spectra of 2-hydroxypyrene in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

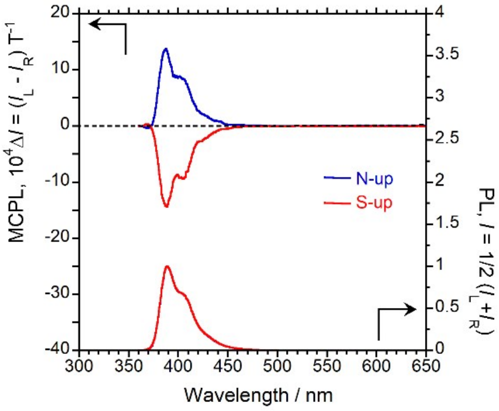


Fig. S18. MCPL and PL spectra of 2-hydroxypyrene in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

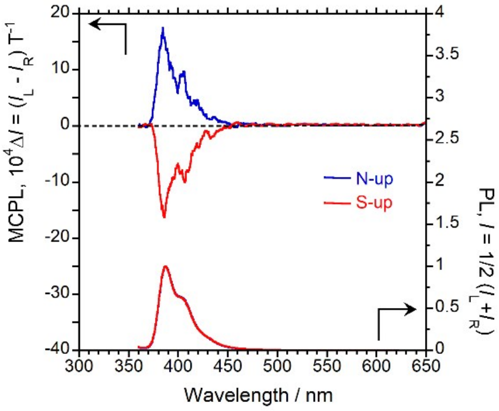


Fig. S19. MCPL and PL spectra of 2-hydroxypyrene in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

5. MCPL and PL spectra of 2-methoxypyrene (2b; 2-PyOCH$_3$) in $CHCl_3$ under an external magnetic field of 1.6 T

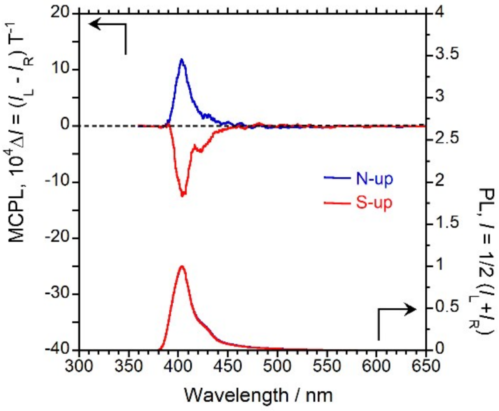


Fig. S20. MCPL and PL spectra of 2-PyOCH$_3$ in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-2} M, path length = 5 mm, 25 °C).

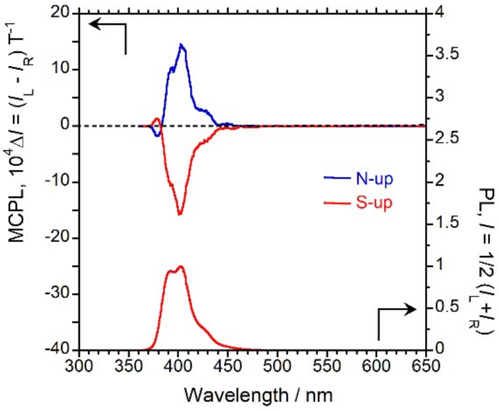


Fig. S21. MCPL and PL spectra of 2-PyOCH$_3$ in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

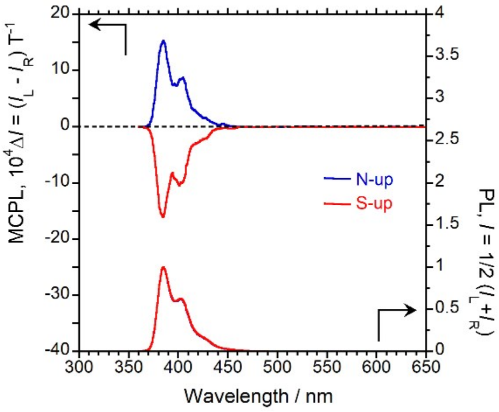


Figure S22. MCPL and PL spectra of 2-PyOCH$_3$ in CHCl$_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

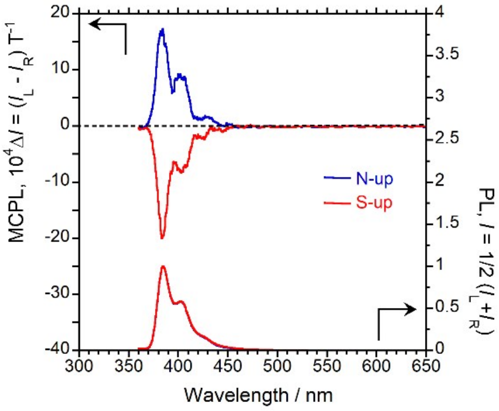


Fig. S23. MCPL and PL spectra of 2-PyOCH$_3$ in CHCl$_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

6. MCPL and PL spectra of 2-Pyrenecarboxylic acid (2c; 2-PyCOOH) in CHCl$_3$ under an external magnetic field of 1.6 T

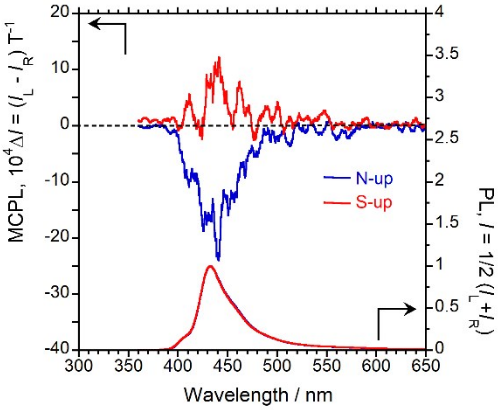


Fig. S24. MCPL and PL spectra of 2-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-2} M, path length = 5 mm, 25 °C).

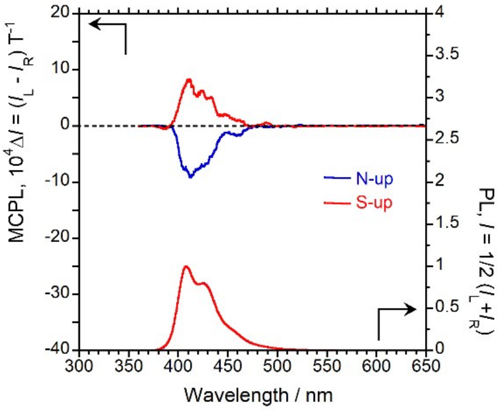


Fig. S25. MCPL and PL spectra of 2-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

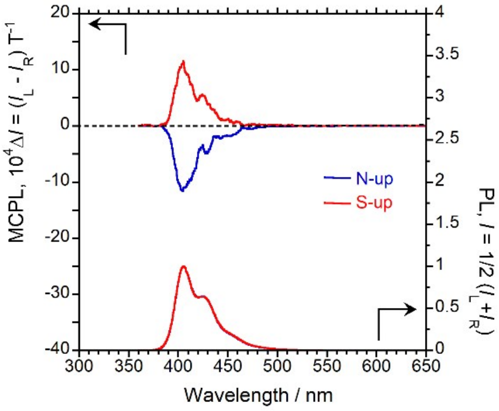


Fig. S26. MCPL and PL spectra of 2-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

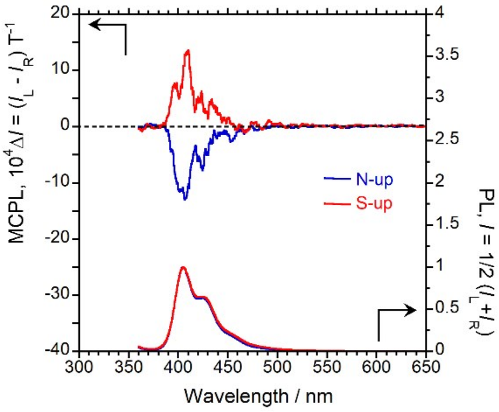


Fig. S27. MCPL and PL spectra of 2-PyCOOH in $CHCl_3$ under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

7. MCPL and PL spectra of 3- hydroxyphenanthrene (3a; 3-PheOH) in THF under an external magnetic field of 1.6 T

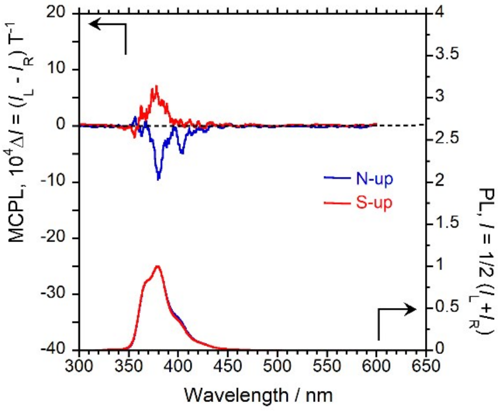


Fig. S28. MCPL and PL spectra of 3-PheOH in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

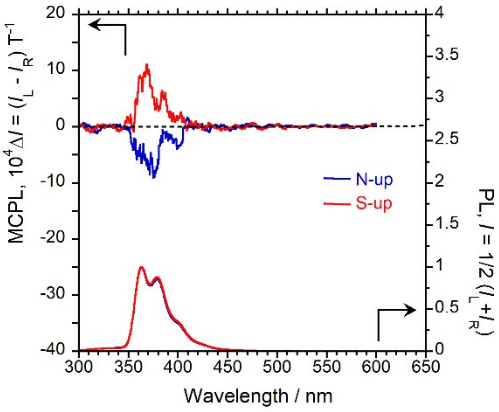


Fig. S29. MCPL and PL spectra of 3-PheOH in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

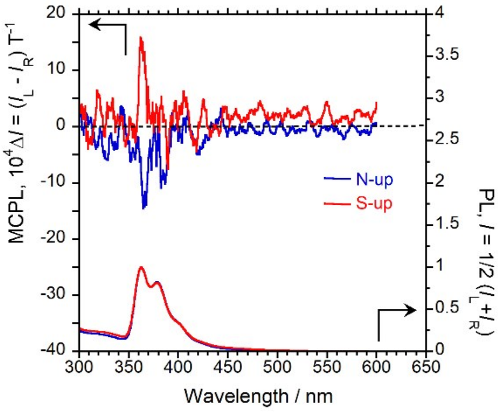


Fig. S30. MCPL and PL spectra of 3-PheOH in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

8. MCPL and PL spectra of 3-methoxyphenathrene (3b; 3-PheOCH$_3$) in THF under an external magnetic field of 1.6 T

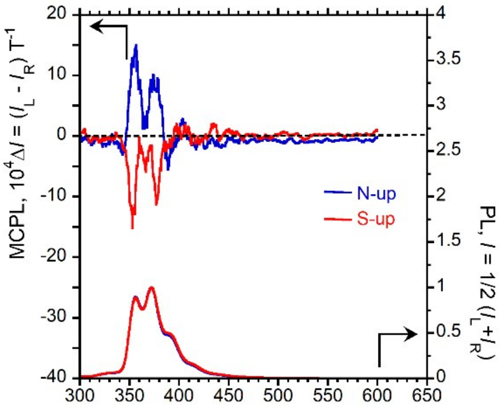


Fig. S31. MCPL and PL spectra of 3-PheOCH$_3$ in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

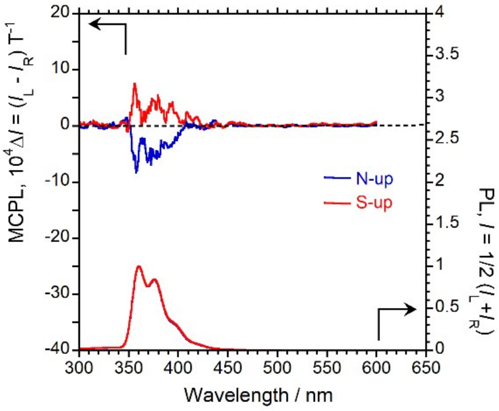


Fig. S32. MCPL and PL spectra of 3-PheOCH$_3$ in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

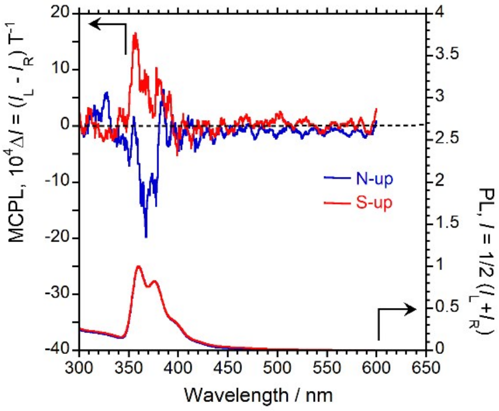


Fig. S33. MCPL and PL spectra of 3-PheOCH$_3$ in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

9. MCPL and PL spectra of 3-phenanthrenecarboxylic acid (3c; 3-PheCOOH) in THF under an external magnetic field of 1.6 T

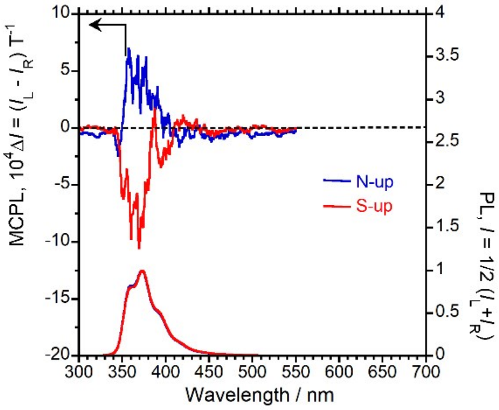


Fig. S34. MCPL and PL spectra of 3-PheCOOH in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-3} M, path length = 5 mm, 25 °C).

Fig. S35. MCPL and PL spectra of 3-PheCOOH in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

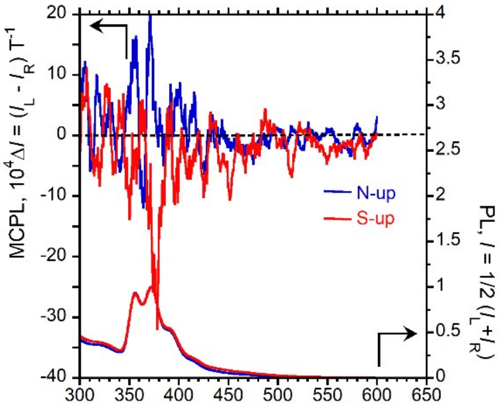


Fig. S36. MCPL and PL spectra of 3-PheCOOH in THF under a 1.6 T magnetic field (conc. = 1.0×10^{-5} M, path length = 5 mm, 25 °C).

10. MCPL and PL spectra of 1-Hydroxypyrene (1a; 1-PyOH) in DMSO under an external magnetic field of 1.6 T

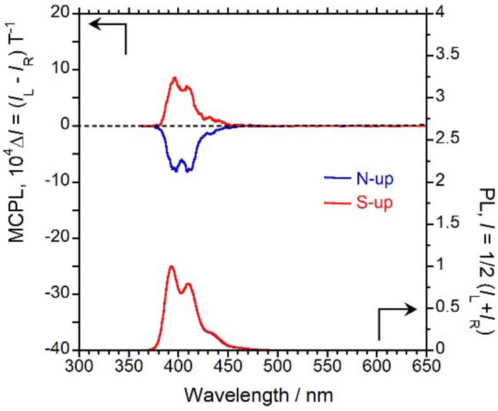


Fig. S37. MCPL and PL spectra of 1-PyOH in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

11. MCPL and PL spectra of 1-Methoxypyrene (1b; 1-PyOCH$_3$) in DMSO under an external magnetic field of 1.6 T

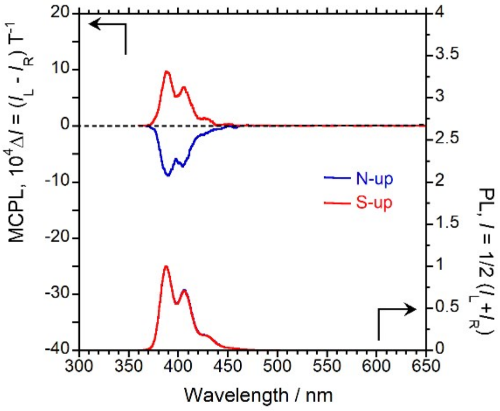


Fig. S38. MCPL and PL spectra of 1-PyOCH$_3$ in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

12. MCPL and PL spectra of 1-Pyrenecarboxylic acid (1c; 1-PyCOOH) in DMSO under an external magnetic field of 1.6 T

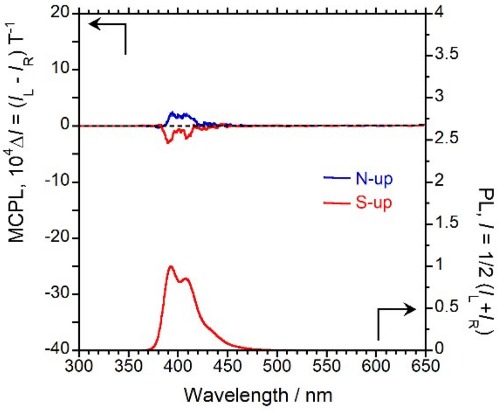


Fig. S39. MCPL and PL spectra of 1-PyCOOH in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

13. MCPL and PL spectra of 2-Hydroxypyrene (2a; 2-PyOH) in DMSO under an external magnetic field of 1.6 T

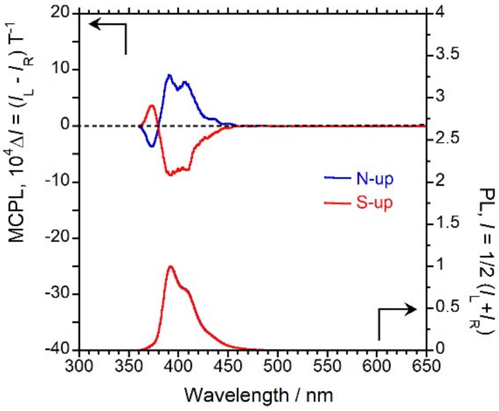


Fig. S40. MCPL and PL spectra of 2-PyOH in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

14. MCPL and PL spectra of 2-Methoxypyrene (2b; 2-PyOCH$_3$) in DMSO under an external magnetic field of 1.6 T

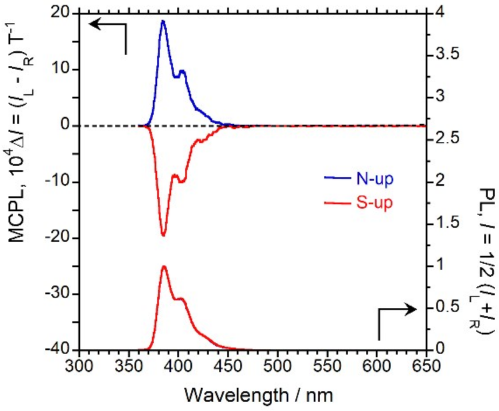


Fig. S41. MCPL and PL spectra of 2-PyOCH$_3$ in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

15. MCPL and PL spectra of 2-Pyrenecarboxylic acid (2c; 2-PyCOOH) in DMSO under an external magnetic field of 1.6 T

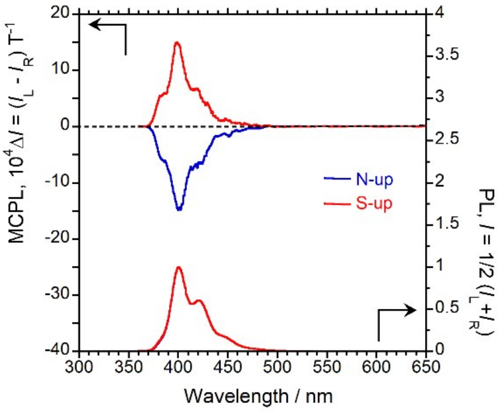


Fig. S42. MCPL and PL spectra of 2-PyCOOH in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

16. MCPL and PL spectra of 3-Hydroxyphenanthrene (3a; 3-PheOH) in DMSO under an external magnetic field of 1.6 T

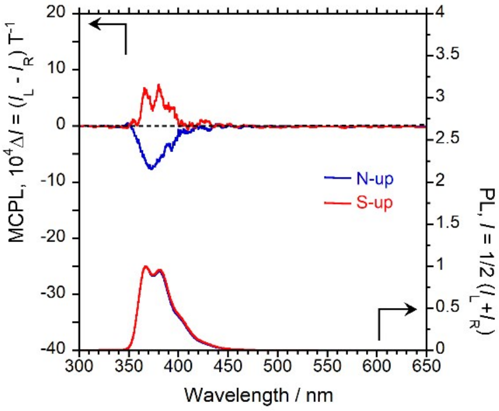


Fig. S43. MCPL and PL spectra of 3-PheOH in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

17. MCPL and PL spectra of 3-Methoxyprenol (3b; 3-PheOCH$_3$) in DMSO under an external magnetic field of 1.6 T

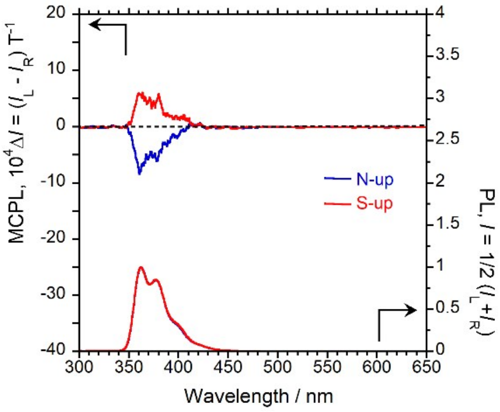


Fig. S44. MCPL and PL spectra of 3-PheOCH$_3$ in DMSO under a 1.6 T magnetic field (conc. = 1.0×10^{-4} M, path length = 5 mm, 25 °C).

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[S2] M. Murai, N. Hosokawa, D. Roy, and K. Takai, *Org. Lett*., **2014**, *16*, 4134-4137.