Supplementary Information

Quantitative Imaging of Magnetic Field Distribution Using a Pyrene-based Magnetosensing Exciplex Fluorophore

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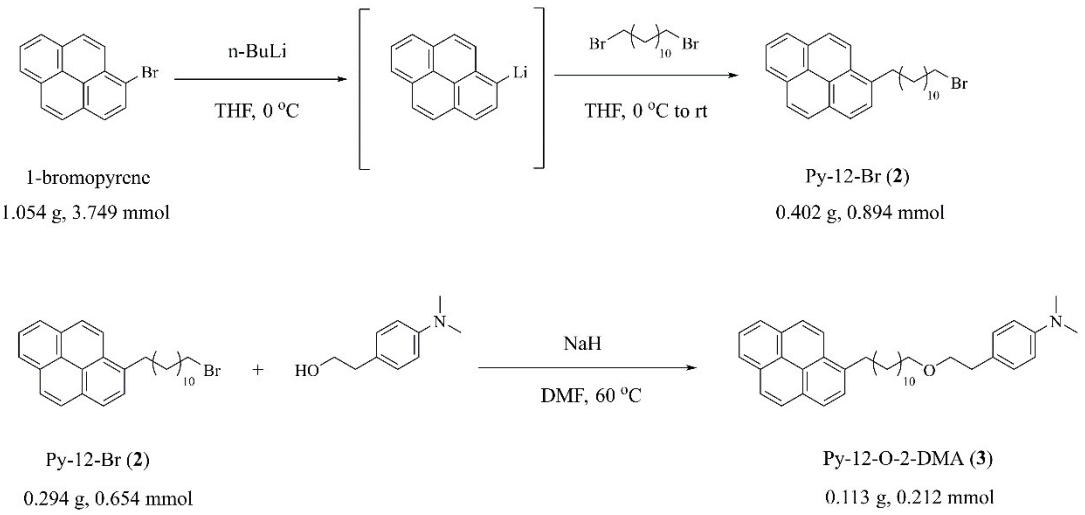
Part 1. Materials



Scheme S1. Preparation of Py-12-O-2-DMA

1. Py-12-Br

Anhydrous tetrahydrofuran (THF, 5 mL) was added to a flame-dried flask containing 1-bromopyrene (1.054 g, 3.749 mmol) under argon. *n*-Butyllithium in hexanes (2.46 M; 1.74 mL, 4.280 mmol) was added to the solution dropwise in an ice-bath. After 20 minutes, a solution of 1,12-dibromododecane (2.340 g, 7.131 mmol) in anhydrous THF (5 mL) was added at 0 ℃. After being stirred at room temperature for 13 hours, a saturated NH_4Cl (aq) solution was added to the reaction mixture. The mixture was extracted by diethyl ether. The extracted organic phase was dried over anhydrous $MgSO_4$, filtered and, concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes) to give 0.4019 g of Py-12-Br (0.894 mmol, 24 %) as yellow solid. Data for Py-12-Br (**2**); m. p.: 74.2 ~ 75.1 ℃; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.29 (d, *J* = 9.2 Hz, 1H), 8.17-8.09 (m, 4H), 8.05-7.97 (m, 3H), 7.87 (d, *J* = 7.6 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 3.34 (t, *J* = 7.8 Hz, 2H), 1.90-1.81 (m, 4H), 1.56-1.27 (m, 16H); ^{13}C NMR (100MHz, $CDCl_3$): δ 137.6, 131.7, 131.1, 129.9, 128.8, 127.8, 127.5, 127.3, 126.7, 126.0, 125.3, 125.0, 124.8, 123.8, 34.3, 33.8, 33.0, 32.2, 30.0, 29.8, 29.7, 29.6, 29.0, 28.4.

2. Py-12-O-2-DMA

2-[4-(Dimethylamino)phenyl]ethanol (0.168 g, 1.017 mmol) in anhydrous *N,N*-dimethylformamide (DMF, 5 mL) was added to a two-neck flask with condenser containing NaH (60% oil suspension; 0.101 g, 2.525 mmol) under argon. The resulting mixture was heated to 60 ℃. A solution of Py-12-Br (0.294 g, 0.654 mmol) in anhydrous DMF (15 mL) was added. After 20 hours, a saturated NH_4Cl (aq) solution was added to the reaction mixture. The mixture was extracted by ethyl acetate. The extracted organic phase was dried over anhydrous $MgSO_4$, filtered and, concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate = 20/1) to give 0.113 g of Py-12-O-2-DMA (0.212 mmol, 32%) as yellow solid. Data for Py-12-O-2-DMA (**3**); m. p.: 39.4 ~ 40.1 ℃. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.29 (d, *J* = 9.2 Hz, 1H), 8.17-8.09 (m, 4H), 8.05-7.97 (m, 3H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.76 (br s, 2H), 3.57 (t, J = 7.6 Hz, 2H), 3.43 (t, J = 6.6 Hz, 2H), 3.34 (t, J = 7.8 Hz, 2H), 2.92 (s, 6H), 2.83-2.78 (m, 2H), 1.90-1.82 (m, 2H), 1.59-1.27 (m, 18H); ^{13}C NMR (100MHz, $CDCl_3$): 149.4, 137.6, 131.6, 131.1, 129.9, 129.7, 128.8, 127.7, 127.4, 127.3, 126.6, 125.9, 125.3, 125.0, 124.8, 123.7, 113.2, 72.5, 71.3, 41.1, 35.5, 33.8, 32.2, 30.0, 30.0, 29.8, 29.8, 29.7, 26.4. HRMS (ESI) for $C_{38}H_{47}NO[M+H]^+$ was found 534.3756 m/z (calc. 534.3736 m/z).

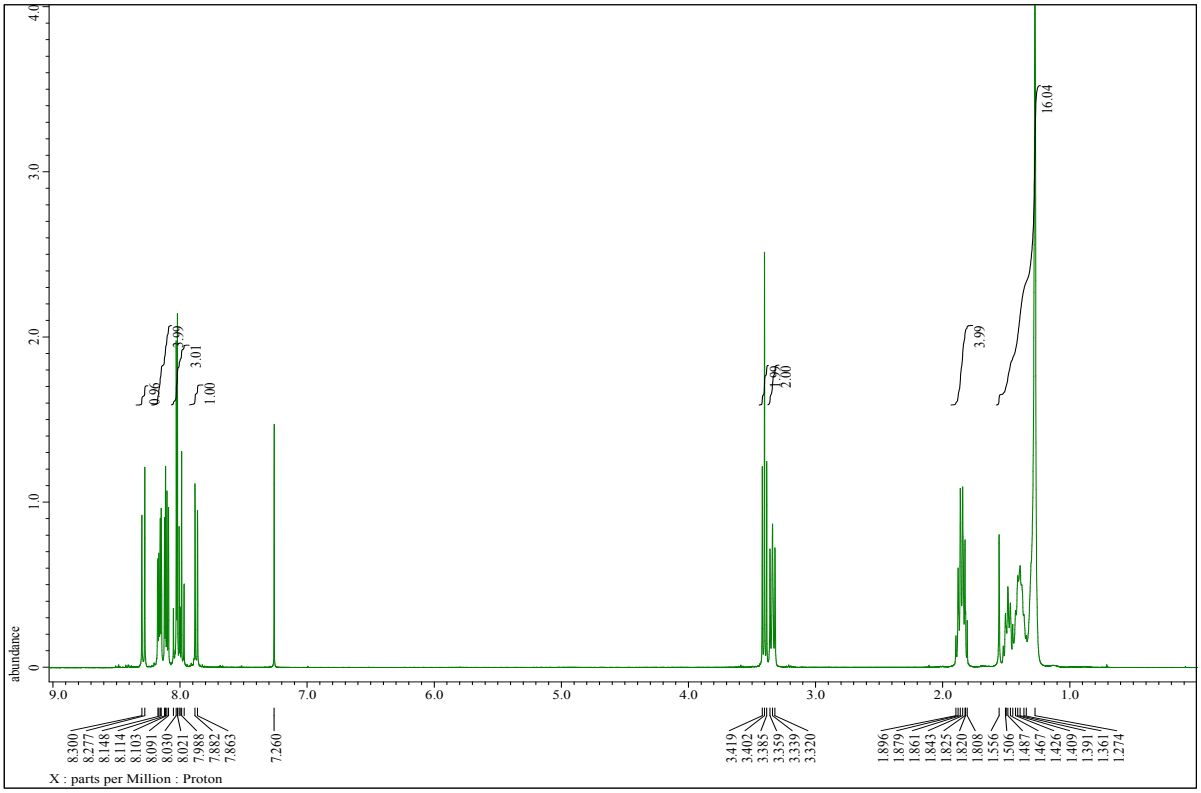


Figure S1. ^{1}H NMR of Py-12-Br (400 MHz, $CDCl_3$).

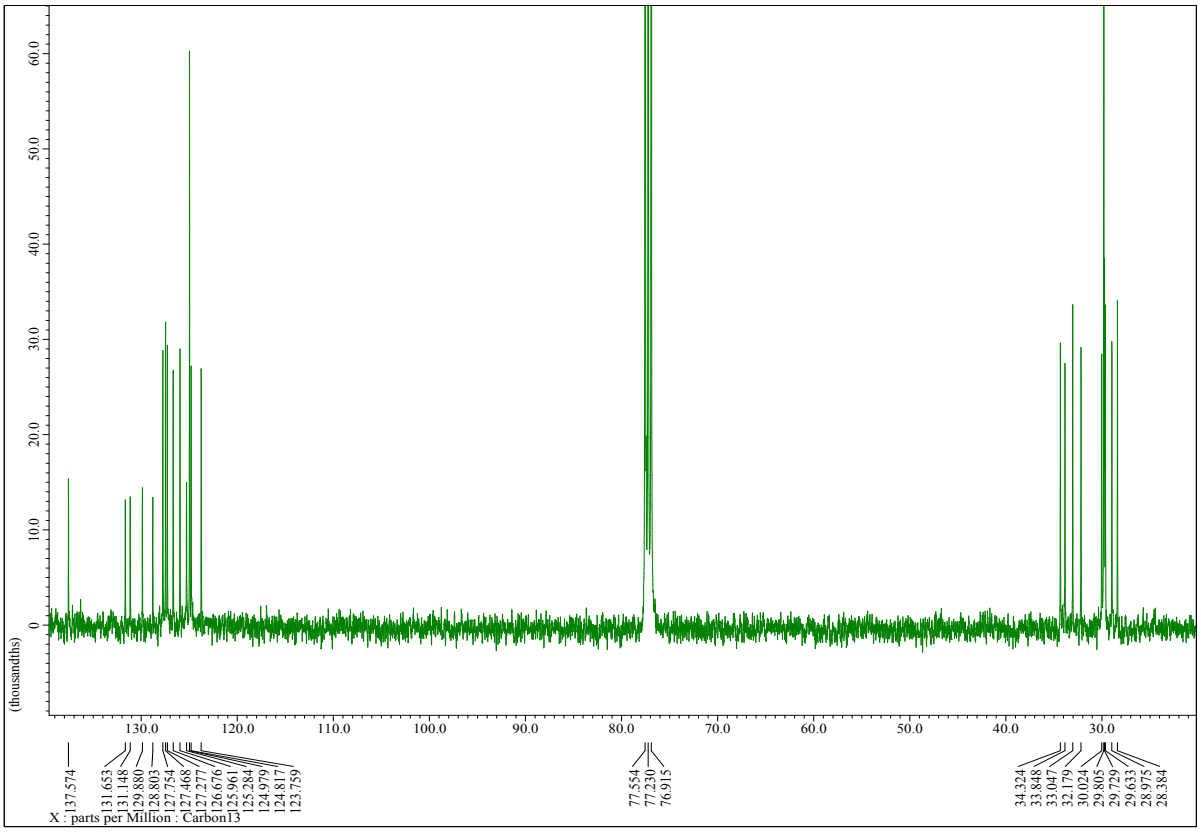


Figure S2. ^{13}C NMR of Py-12-Br (100 MHz, $CDCl_3$).

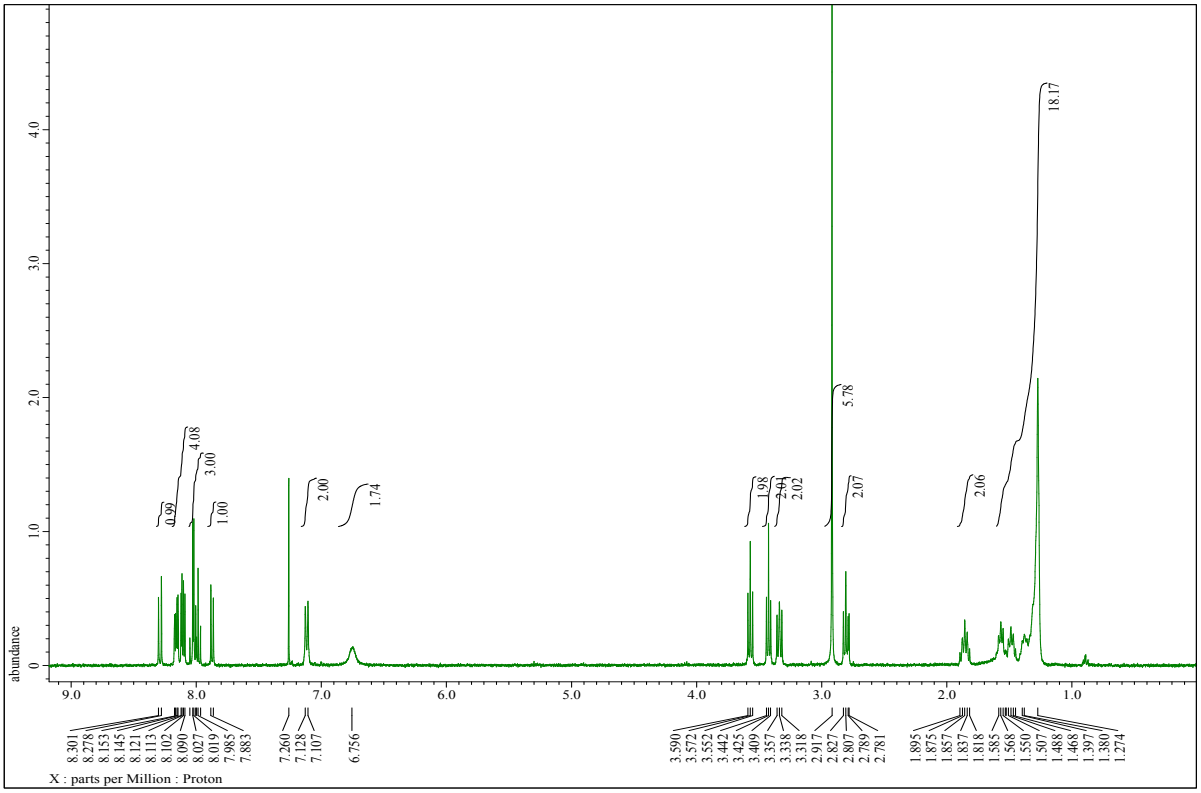


Figure S3. ^{1}H NMR of Py-12-O-2-DMA (400 MHz, $CDCl_3$).

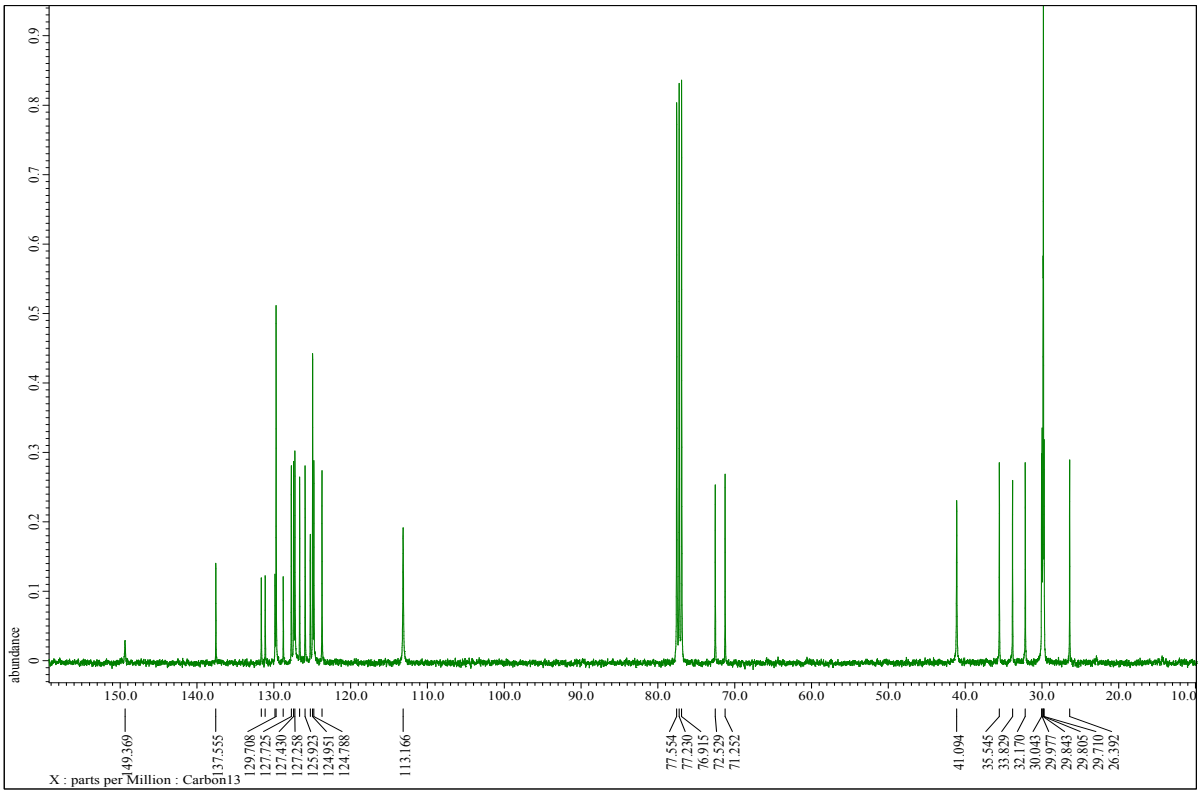


Figure S4. ^{13}C NMR of Py-12-O-2-DMA (100 MHz, $CDCl_3$).

Part 2. Experimental

1. Emission Measurement with One-Photon Excitation (1PE)

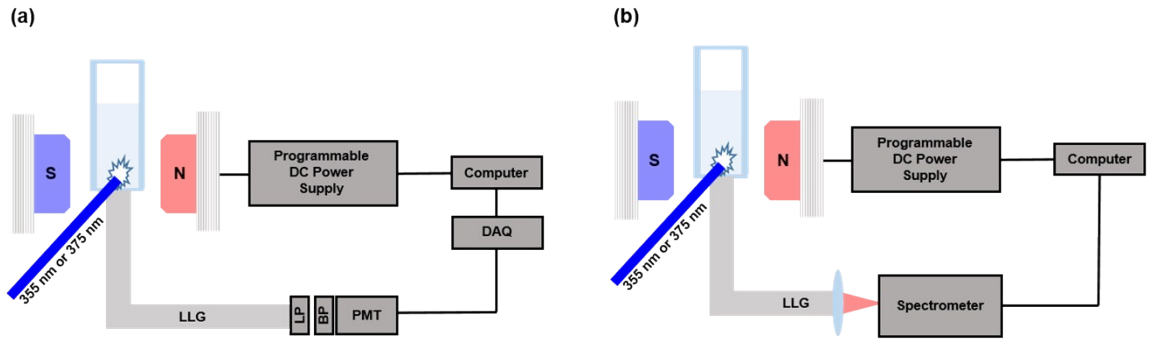


Figure S5. Two schematic diagrams of optical set-up for emission with one-photon excitation (1PE). The emission through the bottom of cuvette was collected and directed by liquid light guide (LLG), either to a photomultiplier tube (**a**) or to a spectrometer **(b)**. 355 nm, Xe arc lamp; 375 nm, LED lamp; LP, longpass filter (450 nm cut-off); BP, bandpass filter 550-600 nm; DAQ, data acquisition device; Spectrometer (FLS980, Edinburgh Instrument).

For the emission measurement with 1PE (**Fig. S5**), the sample solution was contained in a cuvette with septum-topped screw cap (3-SOG-10-GL14-S, Starna) and purged with Ar gas (99.999 %) for at least 20 min before each measurement. The cuvette was placed between the two poles of C-shape electromagnet (Keum-Ryong Tech.) operated by programmable bipolar power supply. For direct comparison of **1** and **3** a 355-nm light extracted from a Xenon arc lamp (XBO450W OFR, Osram Sylvania) was used for illumination. For the other measurement of emission from **3**, 375-nm LED lamp (M375L4, Thorlabs) centered at 375 nm with 8 nm spectral width was used for illumination. The emission was collected by the liquid light guide (LLG0338, Thorlabs) through the bottom window of the cuvette and directed either to PMT (H11526-20-NF, Hamamatsu, Fig. S5a) or to a spectrometer (FLS-980, Edinburgh Instrument). A longpass filter (450 nm cut-off, Knight Optical) and a bandpass filter (#86-952, Edmund Optics) centered at 575 nm with 50-nm FWHM were placed in front of the PMT to allow only exciplex emission and to block the others including illumination scattering and locally excited emission. The power supply for the electromagnet and the PMT were synchronized by a DAQ board (National Instrument) and controlled by LabView code on a personal computer.

2. Emission Measurement with Two-Photon Excitation (2PE)

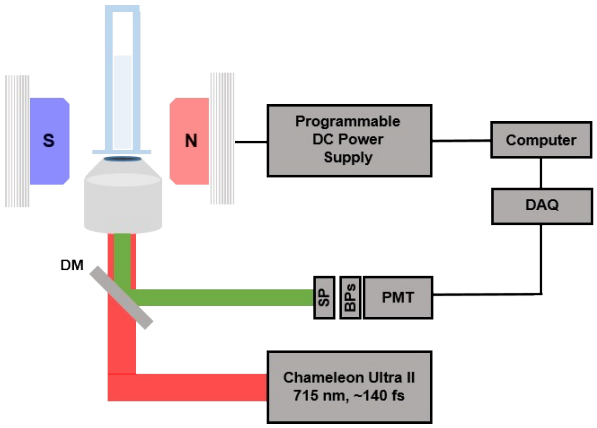


Figure S6. A schematic diagram of optical set-up for the emission measurement with two-photon excitation (2PE). PMT, photomultiplier tube; BPs, a bandpass filter 450-650 nm and the other bandpass filter 550-600 nm; SP, shortpass filter (cut off 650 nm cut-off); DM, longpass dichroic mirror (660 nm cut-off); 60x/1.20w, 60x water immersion objective NA 1.20.

For the emission measurement with 2PE (**Fig. S6**), the sample solution was contained in a customized 130 μm tick coverslip-bottomed sample cell and purged with Ar gas (99.999 %) during each measurement. The sample cell was placed between the two poles of C-shape electromagnet (Keum-Ryong Tech) operated by programmable bipolar power supply. Femtosecond laser pulses (wavelength 715 nm, FWHM ~140 fs, repetition rate 80 MHz, Chameleon Ultra II, Coherent) were focused on the sample cell through a 60x water immersion objective (UplanSApo 60xw / NA 1.2, Olympus). A 660-nm longpass dichroic mirror (T660lpxrxt, Chroma) separated the emission from scattered excitation. The emission was collected by the objective. A 650-nm shortpass filter (FES0650, Thorlabs), a bandpass filter (FF01-550/200-25, Semrock) centered at 550 nm with 200-nm FWHM and a bandpass filter (#86-952, Edmund Optics) centered at 575 nm with 50-nm FWHM were used to allow only exciplex emission and to block illumination scattering in front of a PMT (H10492-013, Hamamatsu). The power supply for the electromagnet and the PMT output were synchronized by a DAQ board (National Instrument) and controlled by LabView code on a personal computer.

3. An image of magnetic field distribution

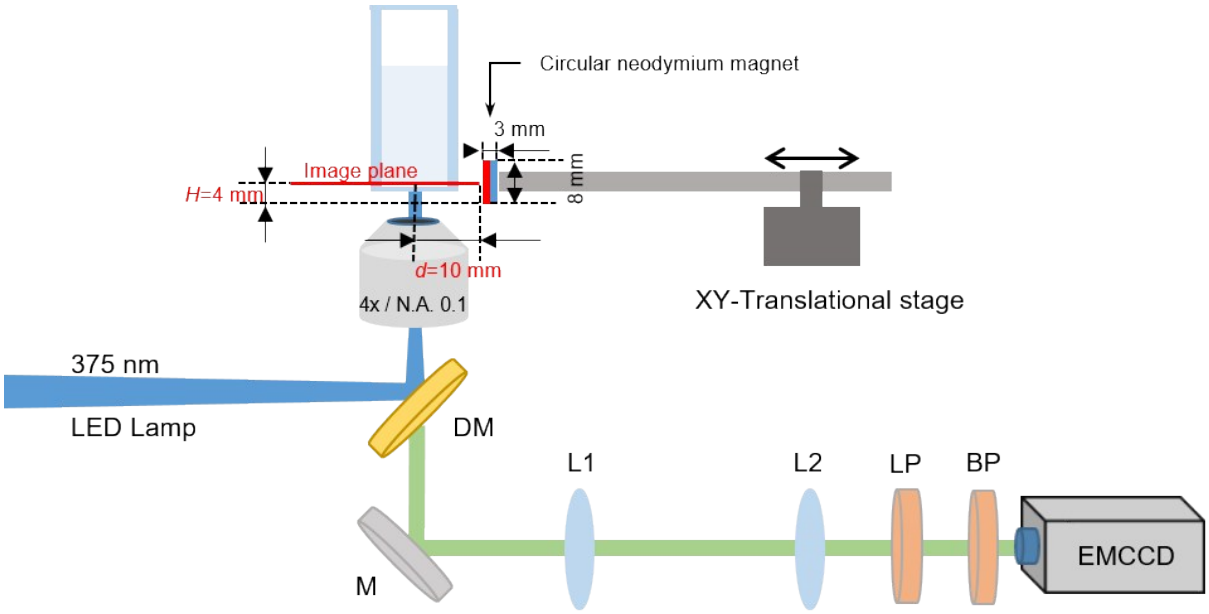


Figure S7. A schematic diagram of optical set-up for a micro-scale image of MFE generated by round-Neodymium magnet. DM, longpass dichroic mirror (420 nm cut-off); M, turning mirror; L1, achromatic lens (focal length: 180 mm); L2, achromatic lens (focal length: 200 mm); LP, longpass filter (450 nm cut-off); BP, bandpass filter 550-600 nm; EMCCD, electron-multiplying CCD camera.

For MFE micro-scale MFE image (**Fig. S7**), a sample solution was contained in a cuvette with septum-topped screw cap (3-SOG-10-GL14-S, Starna) and purged with Ar gas (99.999 %) for at least 20 min before each measurement. The sample solution contained in the cuvette was illuminated by 375-nm LED-lamp (M357L4, Thorlabs) centered at 375 nm with 8-nm spectral width via an inverted epifluorescence microscope (IX73, Olympus) with a 4 X objective (PLN4x NA 0.10, Olympus). To separate exciplex fluorescence from scattered illumination light and locally excited emission from Py* we used a dichroic mirror (420lpxr, Chroma) and the emission filters, a longpass filter (450 nm cut-off, Knight Optical) and a bandpass filter (#86-952, Edmund Optics) centered at 600 nm with 50-nm FWHM. An emission collected by the objective was focused on an EMCCD camera (iXon 897, Andor) by two consecutive achromatic lenses (focus lengths, 180 mm and 200 mm). A round-neodymium magnet (Φ: 8 mm, thickness: 3 mm) was placed to the side of a cuvette. A distance between the

surface of the magnet and a center of microscopic field of view (FOV) was manipulated by XY-translational stage. In order to observe the decay of the MFE in the FOV we set the distance to 10 mm.

Part 3. Result and Discussion

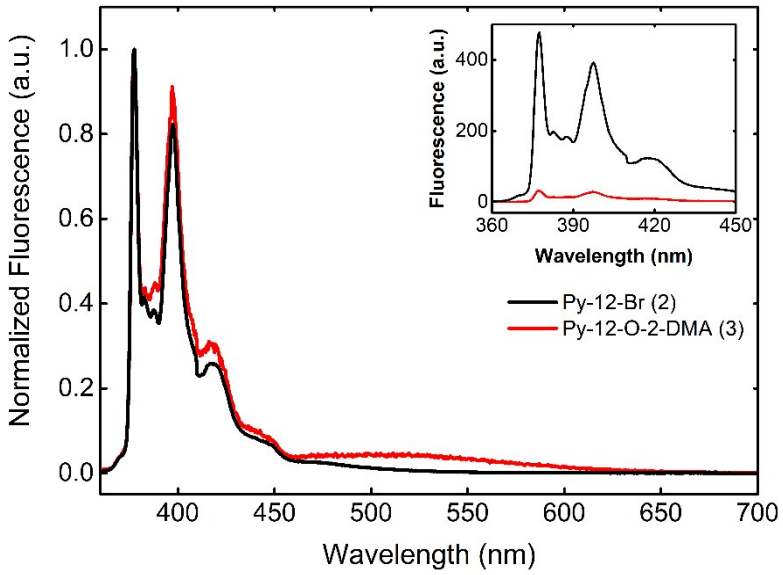


Figure S8. Normalized and un-normalized (inset) fluorescence spectra of Py-12-O-2-DMA (red line) and Py-12-Br (black line) at 10^{-4} M in anisole:DMF = 50:50 (v/v). Excitation wavelength is 355 nm.

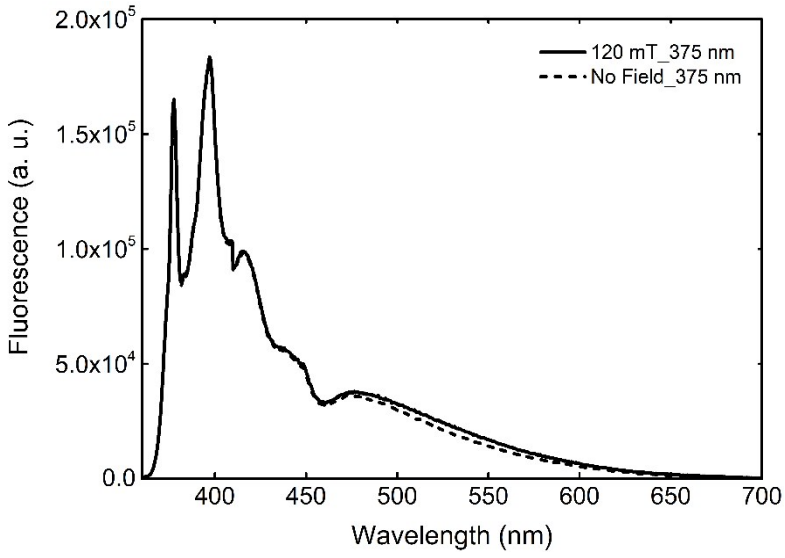


Figure S9. Magnetic field effect on the emission spectrum of Py-12-O-2-DMA (10^{-4} M, anisole:DMF = 50:50 (v/v)). Excitation wavelength is 375-nm LED lamp.

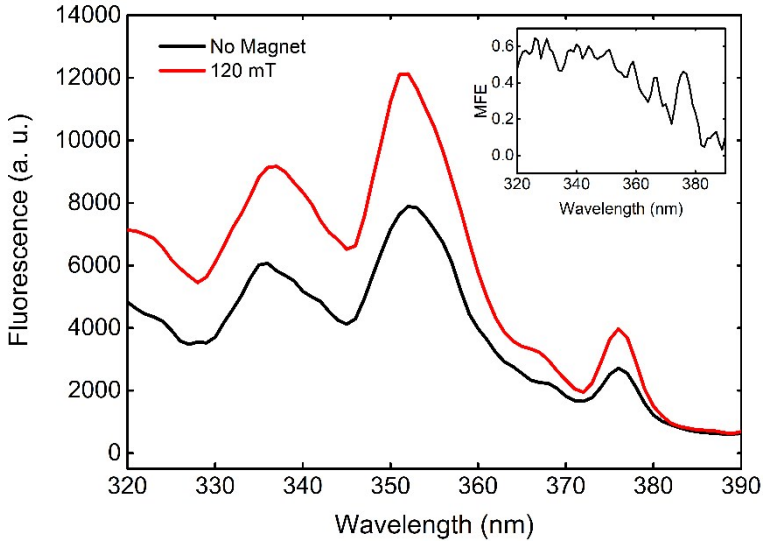


Figure S10. Excitation spectrum at 527 nm, center wavelength of the exciplex emission, (Py-12-O-2-DMA, 10^{-4} M, anisole: DMF = 50:50 (v/v)) affected by magnetic field (black solid line: without magnetic field, red solid line: with magnetic field (120 mT)). Inset: Magnetic field effect on the excitation spectrum. The mean value of MFE between 371 and 379 nm is 0.34.

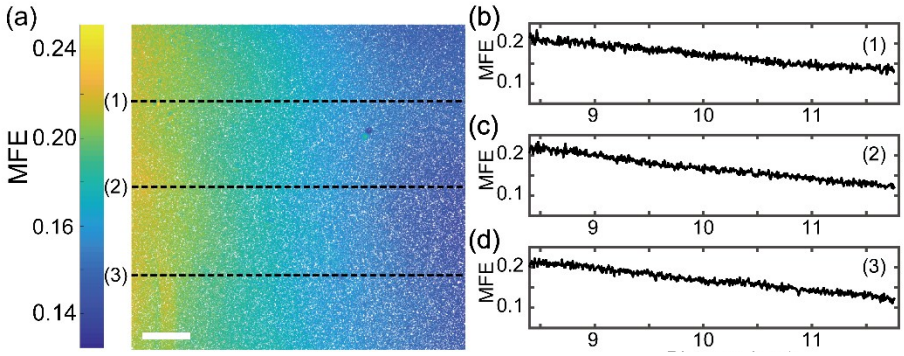


Figure S11. (a) An image obtained by epifluorescence microscopy shows the spatial distribution of MFE resulted from magnet 10 mm away from the center of the field of view. Scale bar is 500μm. **(b)**, **(c)**, and **(d)** are cross-sections of the image in dashed lines ((1), (2), and (3)), respectively.

From MFE-B curve of **Fig. 4(a)** in the main text, we calculated a cubic equation (**Eqn. S1**) by polynomial curve fitting in MATLAB. The result of the cubic equation is in good agreement with the MFE-B curve of **Fig. 4(a)** (**Fig. S12**).

$$Field\ Strength = 0.05791(MFE)^3 - 2.612(MFE)^2 + 46.79(MFE) - 182.4 \qquad \textbf{(Eqn. S1)}$$

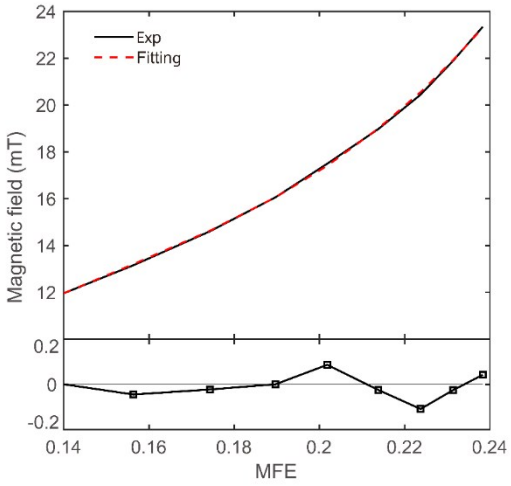


Figure S12. The top plot shows that the conversion through **Eqn. S1** match with the experimental result (MFE-B curve, **Fig. 4(a)**). The bottom plot shows residuals from the top plot.

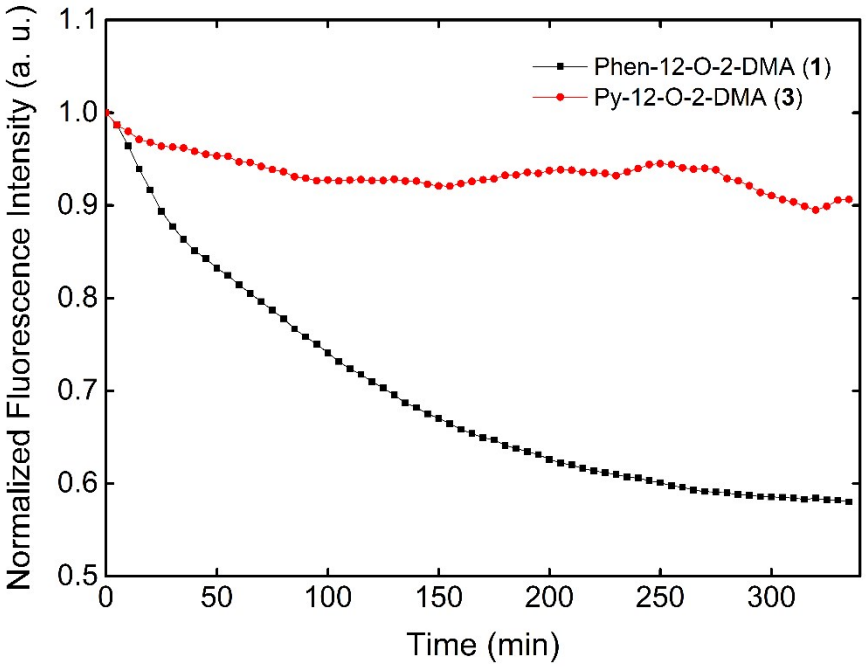


Figure S13. The photostability curves of **1** and **3** with the 355-nm CW laser excitation. The excitation laser powers were set such that their exciplex emission integrated between 450 and 600 nm are same, ca. 1800 mW/cm^2 and 120 mW/cm^2, respectively. 0.5 mL 10^{-4} M of **1** and **3** were contained in a 1 cm x 1 cm quartz cuvette with a septum-topped screw cap and the excitation laser beam diameter was 700 μm. The samples were Ar-purged. The emission spectra were taken at every 5 min. on a fluorescence spectrometer (FLS980, Edinburgh Instrument) and the area between 450 nm and 600 nm was estimated and normalized at 0 min. **1** bleaches about 40 % in 300 min. whereas **3** bleaches less than 10 % in the same excitation time.

Table S1. Transmittance of N-BK 7[a] to the wavelength of transmitted light.[b]

Thickness [c]	300 nm [d]	350 nm [d]	380 nm [d]
25 mm	**0.050**	**0.920**	**0.983**

[a] SCHOTT N-BK7R of SCHOTT AG (Advanced Optics, Hattenbergstrasse 10, 55122 Mainz, Germany);

[b] Schott AG, Optical Glass Data Sheets, https://www.schott.com/d/advanced_optics/ac85c64c-60a0-4113-a9df-23ee1be20428/1.5/schott-optical-glass-collection-datasheets-english-17012017.pdf;

[c] Thickness of optical material: N-BK 7;

[d] Wavelength of transmitted light;

Table S2. Results of fluorescence spectra measurements of Py-12-O-2-DMA[a] and Phen-12-O-2-DMA[b] in the same measurement condition [c].

Fluorophores	Exciplex emission's without magnetic field [d]	Enhanced exciplex emission [e]	STD [f]	*S/N* [g]
Py-12-O-2-DMA	**1986426**	**669620**	**6547**	**102.3**
Phen-12-O-2-DMA	**80327**	**28300**	**814**	**34.8**

[a] 10^{-4} M in anisole / DMF = 50 /50;

[b] 10^{-4} M in DMF;

[c] Number of repeated measurements – 10 / Integration range in the spectra – 460~600 nm;

[d] Average of exciplex emission's without magnetic field;

[e] Average of enhanced exciplex emission due to magnetic field;

[f] Standard deviation of enhanced exciplex emission due to magnetic field;

[g] Signal to noise ratio: Enhanced exciplex emission / STD;