Electronic Supplementary Information

Phosphorescence from a pure organic fluorene derivative in solution at room temperature

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Experimental Section

Chemicals and Reagents. All chemicals were purchased from Aldrich, Kanto Chemicals, TCI or Wako and used as received. Chloroform (CHCl₃), anhydrous DMF, and hexane spectroscopic grade (Wako Pure Chemical Industries, Ltd.) were used for analysis. Fluorene derivatives were synthesized according to the literature procedures.^{S1}

General Method. ¹H NMR spectra were recorded on a Biospin DRX-600 spectrometer (600 MHz); chemical shifts are expressed in ppm relative to TMS (0 ppm). UV-Vis absorption spectra, fluorescence spectra spectra were obtained on a Hitachi U-2900 spectrophotometer and Hitachi F-7000 spectrophotometer, respectively. Fluorescence quantum yields were obtained on a Hamamatsu Photonics, Absolute PL Quantum Yield Measurement System, C9920-02G.

Luminescent Lifetime Measurements. The fluorescence and phosphorescence lifetimes of the fluorene derivatives were measured by a Horiba FluoroCube time-correlated single-photon-counting (TCSPC) system equipped with a pulse laser. The decay profile simulations were performed by a nonlinear least-squares method.

Synthesis of CHO–FL–CHO. To a stirred solution of 2,7-dibromo-9,9didodecylfluorene (5 g, 7.6 mmol) in anhydrous ether (50 mL) at –78 °C, 2.5 M *n*-BuLi solution in hexane (7.6 mL, 19.0 mmol) was added dropwise under argon atmosphere and continued stirring for 30 min. The reaction mixture was warmed to room temperature and kept stirring for another 30 min. The mixture was cooled again to – 78 °C, followed by the addition of DMF (2.1 mL, 27.1 mmol). The mixture was then stirred at –78 °C for 30 min, warmed to room temperature gradually, and stirred for 1 h. Aqueous HCl solution (2 M, 80 mL) was added and continued stirring for another 2 h. The reaction mixture was extracted with ether and washed with water and brine. The organic extracts were dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to give white solid. Yield: 83%; ¹H NMR (600 MHz, CDCl₃): δ [ppm]

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0.53–0.57 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 6H), 1.02–1.31 (m, 36H), 2.05–2.11 (m, 4H), 7.90–7.94 (m, 6H), 10.10 (s, 2H).

Preparation of Fluorene-Doped Films. The fluorene derivatives (5 mmol) and PMMA (500 mg) were dissolved in 10 mL of CHCl₃, and the solution was drop-casted onto the surface of quartz cell. The transparent PMMA films of the fluorene derivatives were obtained by slow evaporation of CHCl₃.

Theoretical calculations. Molecular orbital calculations were carried out with TDDFT^{S2} employing B3LYP hydrid functional^{S3} and 6-31G* basis set using Gaussian 03 program package.^{S4} The molecular geometry was fully optimized in all calculations at S_0 and T_1 states. All other excited states were evaluated using the geometry at S_0 . HOMO–1 means the orbital next to HOMO.

References:

- (S1) C. Vijayaku mar, K. Sugiyasu and M. Takeuchi, Chem. Sci., 2011, 2, 291.
- (S2) R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett., 1996, 256, 454.
- (S3) A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- (S4) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, 2009, Revision A.01*, Gaussian Inc., Wallingford CT.



Fig. S1 UV-Vis absorption of (a) FL, (b) Br–FL–Br, and (c) CHO–FL–CHO in CHCl₃ (4×10^{-5} M) at 298K.



Fig. S2 Fluorescence spectra of Br–FL–CHO (4 × 10^{-5} M) in (a) hexane and (b) DMF under air (red dashed line) and Ar (blue line) at 298K ($\lambda_{ex} = 300$ nm).



Fig. S3 (a) UV-Vis absorption spectrum and (b) excitation spectrum of Br–FL–CHO $(4 \times 10^{-5} \text{ M})$ at 500 nm in CHCl₃ at 298 K.



Fig. S4 (a) Concentration dependence of phosphorescence intensity of [Br–FL–CHO] at 500 nm in CHCl₃ at 298 K. (b) Comparison of ¹H NMR spectra of [Br–FL–CHO] at 1×10^{-2} M (upper) and 1×10^{-4} M (lower) in CDCl₃ at 298 K.



Fig. S5 Emission lifetime of Br–FL–CHO (red: 4×10^{-5} M) and instrumental response function (black: IRF) observed at 370 nm in CHCl₃ at 298 K. The solid line is a fitted line for the fluorescence emission of Br–FL–CHO. Excitation wavelength is 333 nm.



Fig. S6 Fluorescence spectrum of Br–FL–CHO in 2-methyltetrahydrofrane at 77 K ($\lambda_{ex} = 332$ nm).



Fig. S7 Emission spectra of (a) FL, (b) Br–FL–Br, and (c) CHO–FL–CHO in CHCl₃ $(4 \times 10^{-5} \text{ M})$ under air (red dashed line) and Ar (blue line) at 298K. Excitation wavelengths are 300 nm (Br–FL–Br and CHO–FL–CHO) and 280 nm (FL).



Fig. S8 Energy diagram of the ground state and the excited states of Br–FL–CHO, evaluated with TDDFT calculations. The molecular orbital pictures of HOMO–1, HOMO, and LUMO are also shown.



Fig. S9 Fluorescence spectra of PMMA films of (a) Br–FL–CHO (dashed line: just after fabricating the film, red line: after 5 days) and (b) FL at 298K. The excitation wavelengths are 300 nm and 280 nm, respectively. (c) Photographic image of PMMA-based Br–FL–CHO (left) and FL (right) upon UV-light irradiation at 254 nm under air at 298 K.