Supporting information

Thermally activated delayed fluorescence from a Zr-based metal-organic framework

Hiroyuki Mieno, Ryota Kabe*, Mark D. Allendorf, and Chihaya Adachi*

1Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan
2JST, ERATO, Adachi Molecular Exciton Engineering Project, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan
3Sandia National Laboratories, Livermore, CA 94551, USA
4International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan
**Experimental**

**Materials**

All starting materials were purchased from commercial suppliers and were used as received. 4,4”-Dimethoxycarbonyl-2’-amino-[1,1’:4’,1”]terphenyl, H$_2$tpdc-NH$_2$, and 2,5-dibromo-\(N,N\)-diphenylaminobenzene (I) were prepared as described in the literature$^{1,2}$.

**Calculations**

All quantum chemical calculations were performed using the Gaussian 09 program package. Geometry optimization was carried out using the B3LYP functional with the 6-31G(d) basis set. Low-lying excited singlet and triplet states were computed using the optimized structures with time-dependent density functional theory (TD-DFT) at the same level.

**Equipment**

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. Elemental analyses (C, H, N) were carried out using a Yanaco MT-5 CHN corder. Solution and thin-film UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 950-PKA UV–vis spectrophotometer. Photoluminescence quantum yields were obtained from an absolute photoluminescence quantum yield measurement system (Quantaurus-QY C11347-01, Hamamatsu Photonics). The photoluminescence decay characteristics of the solution samples were recorded using a fluorescence lifetime measurement system (Quantaurus-Tau, Hamamatsu Photonics). The photoluminescence decay characteristics of the film samples were recorded under vacuum using a streak camera (C4334, Hamamatsu Photonics) equipped with a N$_2$ gas laser (KEN-X, Usho, $\lambda = 337$ nm, pulse width $\approx 500$ ps, repetition rate = 20 Hz) as the excitation source. Emission decay profiles longer than 10 ms were obtained using a multi-pixel photon counter (C13366-1350GA, Hamamatsu photonics) connected with an oscilloscope (DSOX2022A, Keysight). Low-temperature measurements were conducted using a cryostat (CRT-006-2000, Iwatani Industrial Gases). X-ray diffraction patterns were obtained using a Rigaku Ultima IV diffractometer with CuK $\alpha$ radiation.
Thermogravimetric analysis data were measured with a rate of 10 °C/min using a Bruker TG-DTA2400SA analyser. The SEM images were measured using a Inspet S50 (FEI). N₂ isotherm was carried out using a BELSORP-max (MicrotracBEL).

**Synthesis**

**Scheme S1.**

\[ \text{4,4''-Dimethoxycarbonyl-2'-diphenylamino-[1,1':4',1'']} \text{terphenyl (2)} \]

To a dioxane (50 mL) solution of 1 (0.60 g, 1.5 mmol), 4-(methoxycarbonyl)-phenylboronic acid (0.6 g, 3.3 mmol), K₃PO₄ (1.27 g, 6.0 mmol) and [1,1'-bis-(diphenylphosphino)ferrocene]dichloropalladium(II) complex with dichloromethane (Pd(dpff)Cl₂·CH₂Cl₂) (0.12 g, 0.15 mmol) were added. The mixture was heated to 100 °C for 2 days under Ar. The resulting solution was cooled to room temperature and extracted with CH₂Cl₂. The organic layer was filtered with celite and concentrated under reduced pressure. The resulting crude product was subjected to silica gel column chromatography (hexane:CH₂Cl₂ = 4:1) to afford 0.43 g of 2 in a 56% yield as a yellowish white solid.

\( ^1H \text{ NMR (500 MHz, CDCl}_3, 25 ^\circ\text{C}): \delta (\text{ppm}) = 8.08 (d, J = 8.2 \text{ Hz, 2H}), 7.80 (d, 8.1 \text{ Hz, 2H}), 7.63 (d, J = 8.2 \text{ Hz, 2H}), 7.60 (s, 1H), 7.54 (d, J = 8.0 \text{ Hz, 1H}), 7.41 (d, J = 8.0 \text{ Hz, 1H}), 7.28 (d, J = 8.2 \text{ Hz, 2H}), 7.08 (t, 4H), 6.88 (d, J = 7.8 \text{ Hz, 4H}), 6.84 (t, 2H), 3.91 (d, J = 28 \text{ Hz, 6H}). \n
\( ^{13}C \text{ NMR: (125 MHz, CDCl}_3, 25 ^\circ\text{C}): \delta (\text{ppm}) = 167.00, 166.88, 147.21, 145.66, 144.31, 144.12, 141.25, 138.92, 132.32, 130.15, 129.27, 129.22, 128.88, 128.51, 128.47, 128.04, 126.95, 124.47, 122.21, 121.83, 52.18, 52.02. \)
\[ \text{MS (MALDI-TOF-MS)}: \text{m/z 512.76 [M]+} \]

Elemental analysis: calcd. for C\(_{34}\)H\(_{27}\)NO\(_4\): C, 79.5; H, 5.30; N, 2.73; found: C, 79.3; H, 5.31; N, 2.70

4,4”-Dicarboxyl-2’-diphenylamino-[1,1’:4’,1”]terphenyl (H\(_2\)tpdc-dpa)

To a dioxane (20 mL) solution of 2 (0.20 g, 0.4 mmol), KOH (0.17 g, 3.0 mmol) in aqueous solution (10 mL) was added and refluxed overnight. The resulting clear solution was cooled to room temperature and treated with hydrochloric acid (concentrated HCl) through an addition funnel with ice bath until the solution reached a pH of 1. Then, the mixture was stirred for another 1 hour. Finally, the precipitate was filtered and dried under vacuum to give H\(_2\)tpdc-dpa as a yellow powder (0.18 g, 93%).

\(^1\text{H NMR (500 MHz, DMSO, 25 °C)}: \delta (ppm) = 12.9 (br, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.75 (m, 5H), 7.57 (d, J = 8.7 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.13 (t, 4H), 6.85 (t, 6H).

\(^{13}\text{C NMR: (125 MHz, CDCl}_3, 25 °C): \delta (ppm) = 167.53, 167.50, 147.26, 145.45, 143.46, 140.97, 138.81, 133.00, 130.55, 129.65, 129.51, 129.44, 128.78, 127.98, 127.25, 122.75, 122.23.

\[ \text{MS (MALDI-TOF-MS)}: \text{m/z 484.69 [M]+} \]

Elemental analysis: calcd. for C\(_{32}\)H\(_{23}\)NO\(_4\): C, 79.2; H, 4.74; N, 2.88; found: C, 79.0; H, 4.87; N, 2.87

**Synthesis of UiO-68-NH\(_2\) and UiO-68-dpa**

In a 6-dram vial, a DMF solution (10 mL) of H\(_2\)tpdc-NH\(_2\) (67 mg, 0.2 mmol) or H\(_2\)tpdc-dpa (97 mg, 0.2 mmol), ZrCl\(_4\) (57 mg, 0.2 mmol), benzoic acid (UiO-68-NH\(_2\): 488 mg, 4.0 mmol; UiO-68-dpa: 122 mg, 1.0 mmol) and water (18 \(\mu\)L) was heated to 70 °C for 3 days. After cooling to room temperature, the precipitates were isolated by centrifugation. The solids were suspended in DMF (20 mL). After standing at room temperature for 1 day, the suspensions were centrifuged and the solvent was decanted off. This treatment was repeated five times to remove the unreacted organic linker. Afterwards the same procedure was performed with ethanol (20 mL \(\times\) 3). The solids were dried at 120 °C for 12 h under reduced pressure.

Elemental analysis of UiO-68-dpa: calcd. for Zr\(_6\)O\(_5\)(OH)\(_3\)(H\(_2\)tpdc-dpa)\(_{5.5}\) \(\cdot\) 11H\(_2\)O:
C, 59.8; H, 3.98; N, 2.18; found: C, 59.3; H, 3.70; N, 2.31
**Figure S1.** HOMO and LUMO distributions of \( \text{H}_2\text{tpdc-NH}_2 \) (left) and \( \text{H}_2\text{tpdc-dpa} \) (right) calculated at the B3LYP/6-31G level.

**Figure S2.** XRD patterns of UiO-68-NH\(_2\) (blue) and UiO-68-dpa (red).
Figure S3. Nitrogen adsorption isotherms of UiO-68-dpa at 77K.

Figure S4. SEM images of UiO-68-dpa with scale bars of (a) 40 μm and (b) 10 μm.
Figure S5. Thermogravimetric analysis of H$_2$tpdc-dpa (blue) and UiO-68-dpa (red).

Figure S6. Fluorescence (blue line) and phosphorescence (red line) spectra of H$_2$tpdc-dpa in THF (10$^{-6}$ M). Fluorescence was measured at room temperature and phosphorescence at 77 K.
Figure S7. Fluorescence spectra of a PMMA doped with H$_2$tpdc-dpa in various concentrations (2 wt%; blue line, 5 wt%; green line, 10 wt%; orange line, 50 wt%; red line).

Figure S8. Room-temperature decay profiles of H$_2$tpdc-dpa–doped PMMA films at various doping concentrations over time scales of 500 ns (a) and 1 s (b). (c)–(e) Prompt and delayed emission spectra of the films in (a) and (b).
**Figure S9.** Excitation intensity dependence of the delayed emission intensity of UiO-68-dpa.

**Figure S10.** (a) UV-vis absorption spectra and fluorescence spectra of H$_2$tpdc-NH$_2$ and UiO-68-NH$_2$. (b) Decay profiles of UiO-68-NH$_2$ at 300 K under vacuum.
**Figure S11.** Decay profiles of UiO-68-dpa at 300 K in air.

**Figure S12.** Emission spectra of UiO-68-dpa in DMF (dimethylformamide; black line), THF (blue line), toluene (blue line), DCB (o-dichlorobenzene; orange line), and CH$_3$CN (acetonitrile; red line) dispersion and solid state (green line).
Figure S13. $^1$H and $^{13}$C NMR spectra of compound 2.
Figure S14. $^1$H and $^{13}$C NMR spectra of $\text{H}_2\text{tpdc-dpa}$. 
References
