Supplementary Material (ESI) for Chemical Communications

Supporting Information

Anthracene Array-Containing Porous Coordination Polymer with Host-Guest Charge Transfer Interactions in Excited States

Daisuke Tanaka, Satoshi Horike, Susumu Kitagawa, Masaaki Ohba, Miki Hasegawa, Yoshiki Ozawa, and Koshiro Toriumi,

Experimental

General. *N*,*N*-dimetylaniline (DMA), *N*-methylaniline (MA) or *N*,*N*-dimethyl-*p*-toluidine (DMPT) were used after vacuum distillation. Other chemicals and solvents used in the syntheses were of reagent grade and used without further purification. Thermogravimetric (TG) analysis were performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 298 and 773 K in a N_2 atmosphere and at a heating rate of 10 $Kmin^{-1}$. UV-vis reflection spectra were recorded on a Perkin Elmer UV/vis/NIR spectrometer Lambda 19. Luminescent spectra were measured on PERKIN ELMER LS50B. Solid-state ^{13}C NMR was measured by JEOL JNM-LA300 spectrometer and standard CPMAS probe at 75.576 MHz. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with CuKα radiation. The adsorption isotherm for N_2 was measured with BELSORP-18 volumetric adsorption equipment from BEL Japan, Inc. Fluorescence quantum yields were measured by the C9920-02 Absolute PL Quantum Yield Measurement System (Hamamatsu photonics K. K.).[1]

Synthesis of 1⊃Solvents and 1. 9,10-anthracenedicarboxylic acid (H_2adc) was prepared according to the literature procedure(see ref. 4 in the article). A MeOH solution (100 ml) of dabco (0.19 g, 1.7 mmol) was added to a DMF solution (100 ml) of H_2adc (0.88 g, 3.4 mmol) and $Zn(NO_3)_2$ $6H_2O$ (1 g, 3.4 mmol). After the mixture was allowed to stand for 12 hour at 60 ºC, a white precipitate of **1**⊃Solvents was collected. The number of solvents in **1**⊃Solvents was determined by elemental analysis and TG analysis (Fig.S1). **1**⊃Solvents was washed with DMF and methanol, and dried at 120 ºC under a vacuum, resulting in dried form **1**. **1** gradually adsorbed water in air. The number of water in fully water-adsorbed form, **1**⊃H_2O, was estimated at 12.5 from TG analysis (Fig.S3). Anal.

Calcd (Found) for **1**⊃Solvents: {$[Zn_2(adc)_2(dabco)](DMF)_{3.6}(MeOH)_{1.8}(H_2O)_{1.8}$} [$C_{50.6}H_{64}N_{5.6}O_{15.2}Zn_2$]: C, 54.04 (53.51); H, 5.74 (5.18); N, 6.97 (7.59), **1**⊃H_2O: {$[Zn_2(adc)_2(dabco)](H_2O)_{12.5}$} [$C_{38}H_{53}N_2O_{20.5}Zn_2$]: C, 45.79 (45.60); H, 5.36 (4.73); N, 2.81 (2.50). Crystals suitable for single-crystal X-ray diffraction structure analysis were obtained by the following procedure. $Zn(NO_3)_2$ $6H_2O$ (0.30 g, 1 mmol) and H_2adc (0.27 g, 1 mmol) were dissolved in DMF (5 mL). After dabco (0.06 g, 0.5 mmol) and MeOH (5 mL) were added to the mixture, it was stirred for 12 h at room temperature, and then a white precipitate was filtered off. The resulting solution, upon heating to 120 ºC for 48 h, produced colorless, brick-shaped crystals.

Synthesis of 1⊃DMA, 1⊃MA and 1⊃DMPT. In a Pyrex reaction tube, dried complex **1** (100mg) was prepared by evacuation at 120 ºC for 6 h; subsequently, it was immersed in DMA (0.5 ml)at room temperature. After excess DMA was completely removed by evacuation at room temperature for 2 h, the reaction tube was filled with nitrogen. **1**⊃MA and **1**⊃DMPT was prepared same way by using MA and DMPT, respectively.

Single Crystal X-ray Diffraction. A single crystal of **1** ⊃ Solvents was mounted on a carbon fiber attached to a closed-cycle helium cryostat. Data were collected at 150 K, under vacuum to measure reflection intensity accurately by reducing air-scattering background, with synchrotron radiation (λ=0.56076 Å) and a MAC Science low-temperature vacuum X-ray camera equipped with an imaging plate (IP) area detector in the BL02B1 beamline at SPring-8. The structure was solved by direct methods (SHELXS-97)[2] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97)[3]. All non-hydrogen atoms except disordered atoms were anisotropically refined, while all hydrogen atoms were placed geometrically and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. Crystal data for **1**⊃ Solvents, C_{19} H_{14} N O_4 Zn, M_r = 385.68, tetragonal, space group *I*4/*mcm*, (#140), a = 15.3480 (11) Å, c = 18.938 (3) Å, V = 4461.1 (9) Å^3, Z = 8, T = 150 K. 3227 reflections measured, 1755 unique, 1429 > 2σ(I) were used to refine 65 parameters, no restraints, $R(R_w)$ = 0.0636 (0.1995), GOF = 1.193.

1 Y. Kawamura, H. Sasabe, C. Adachi, *Jpn. J. Appl. Phys.* 2004, **43**, 7729
2 Sheldrick, G. M. *SHELXS-97*, Universität-Gottingen, 1997
3 Sheldrick, G. M. *SHELXL-97*, Universität-Gottingen, 1997.

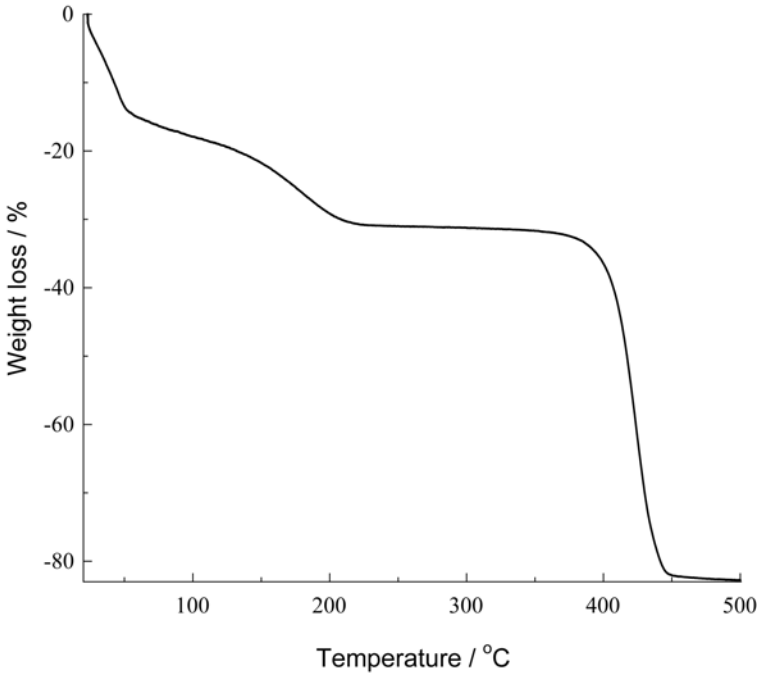

Fig. S1 TG analysis showing the weight loss in **1**⊃Solvents**.** The observed weight loss (31.1%) is the weight of 3.6 DMF, 1.8 MeOH and 1.8 water molecules (calcd: 31.4%).

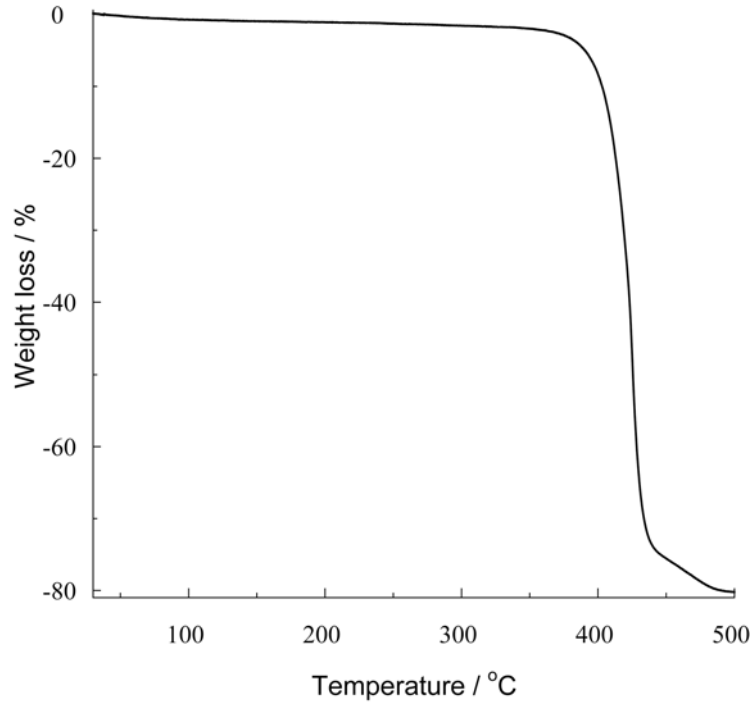

Fig. S2 TG analysis showing the weight loss in dried form, **1**.

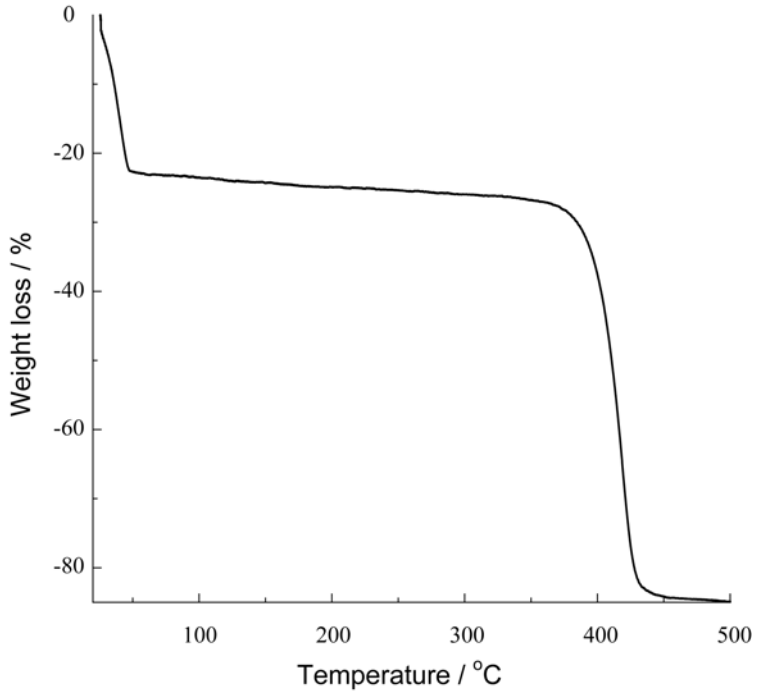

Fig. S3 TG analysis showing the weight loss in **1**⊃H_2O adsorbed water in air. The observed weight loss (22.8%) is the weight of 12.5 water molecules (calcd: 22.6%).

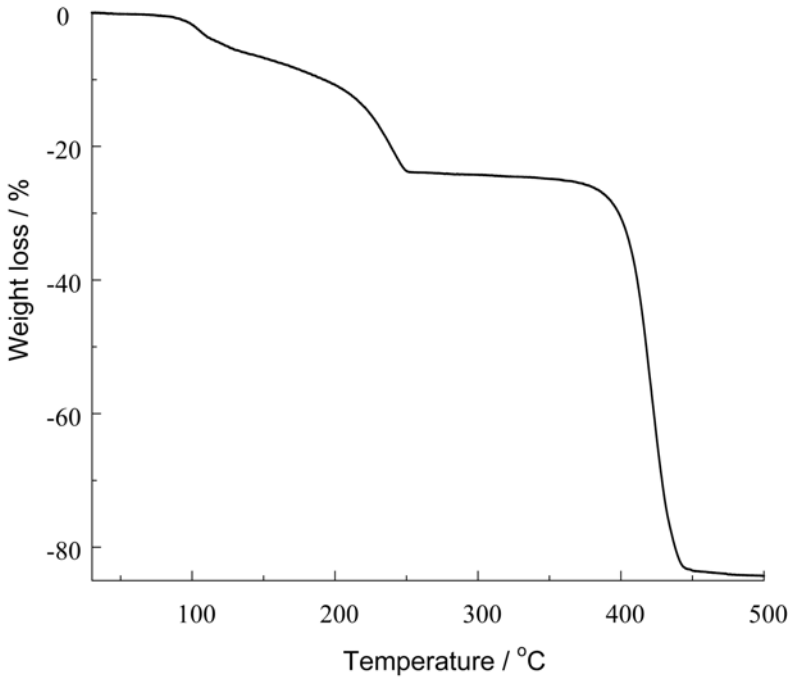

Fig. S4 TG analysis of DMA adsorbed form, **1**⊃DMA. The observed weight loss (24.2%) is the weight of 1.02 DMA molecules

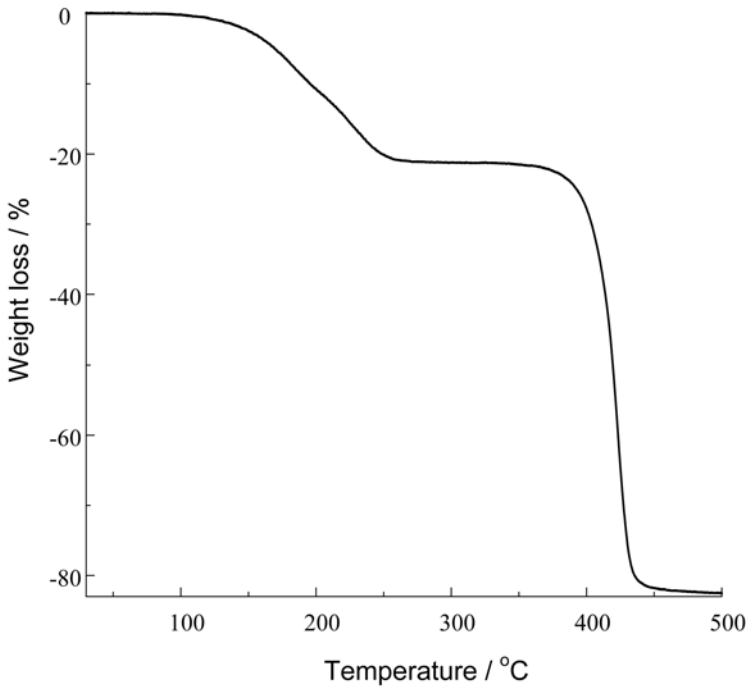

Fig. S5 TG analysis of MA adsorbed form, **1**⊃MA. The observed weight loss (21.2%) is the weight of 0.97 MA molecules

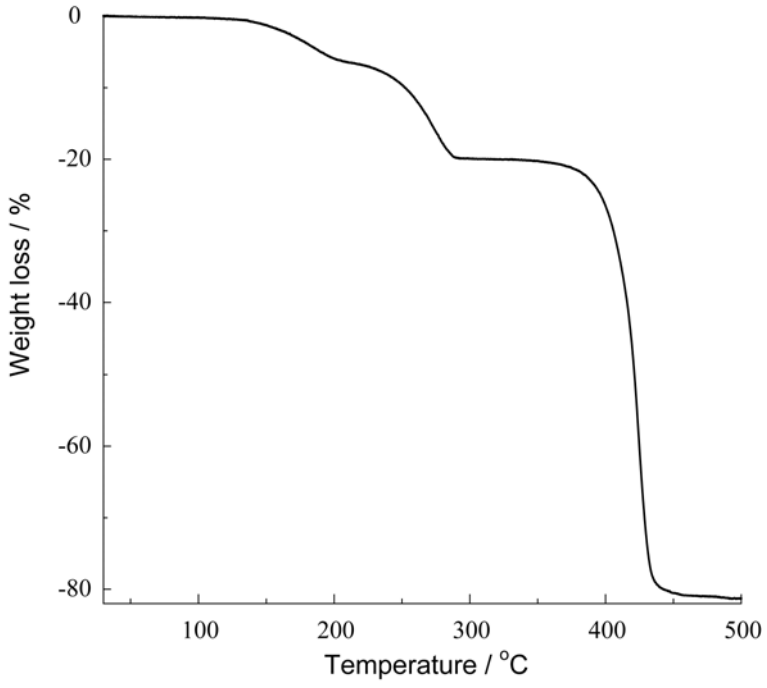

Fig. S6 TG analysis of DMPT adsorbed form, **1**⊃DMPT. The observed weight loss (20.0%) is the weight of 0.71 DMPT molecules

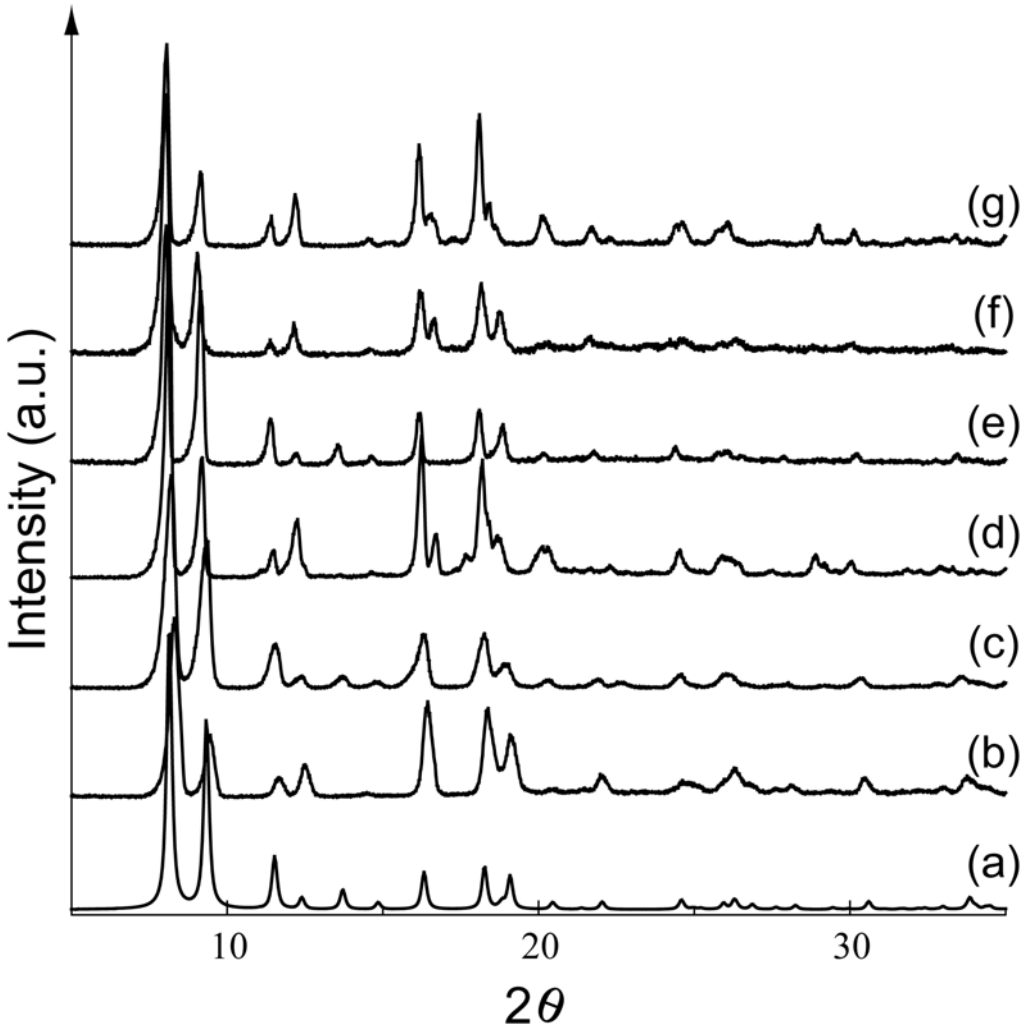

Fig. S7 XRPD patterns of (a) simulated **1**⊃Solvents from single crystal, (b) experimental as synthesized form **1**⊃Solvents, (c) dried form, **1**, (d) **1**⊃DMA, (e) **1**⊃DMA after heating at 350 ºC, (f) **1**⊃MA and (g) **1**⊃DMPT.

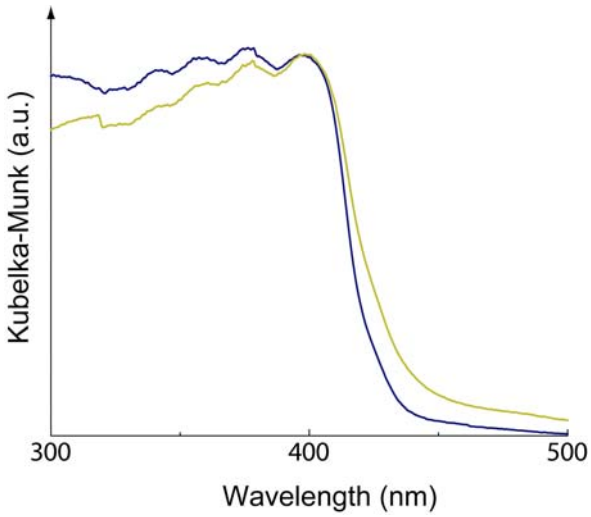

Fig. S8 Diffuse reflectance UV-vis spectra of **1**⊃MA (blue) **1**⊃DMPT (dark yellow)

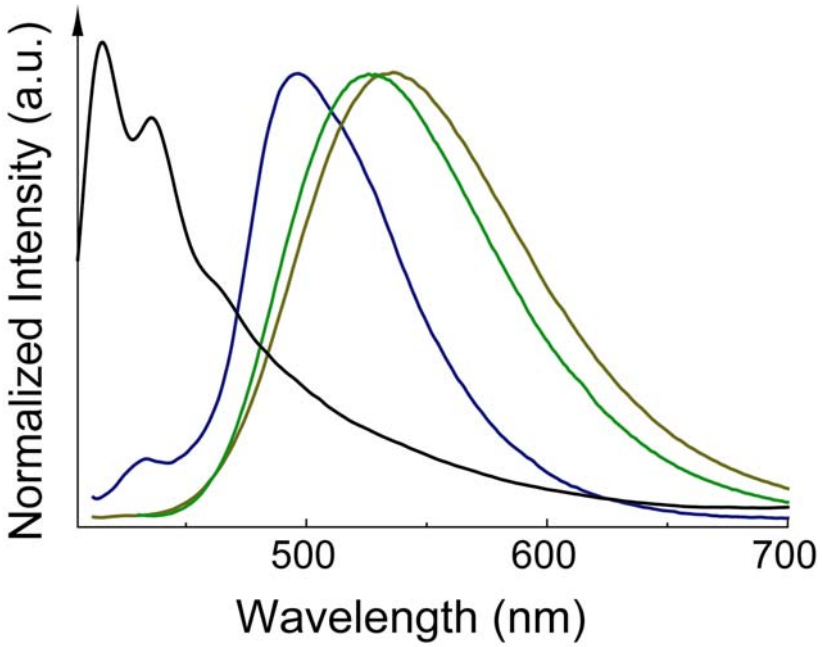

Fig. S9 Emission spectra of dried form, **1** (blue), **1**⊃MA (blue), **1**⊃DMA (green), and **1**⊃DMPT (dark yellow). The excitation wavelengths are 376 nm, 395 nm, 410 nm and 392 nm, respectively.

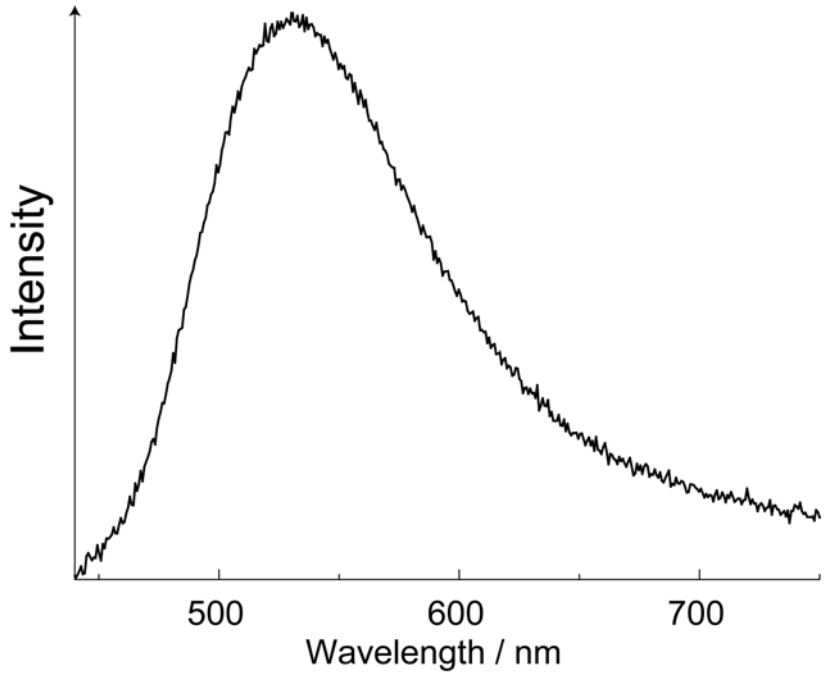

Fig. S9 Emission spectra of **1**⊃DMA for fluorescence quantum yield measurement. The excitation wavelength is 380 nm.