

Supporting Information

Two-photon pumped emission of polymeric thin film doped with dicyanopyranone derivative

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1. Experimental

(1) Synthesis of 1. The synthesis of **1** was according to literature¹ and the detailed procedures were as follows: (a) To a solution of 2,6-dimethyl-4H-pyran-4-one (3.42g, 27.6 mmol) and malononitrile (1.82g, 27.6 mmol) in dry ethanol (150 mL) is added piperidine (23 mg, 0.276 mmol). The solution is stirred at 60°C till starting material disappeared (detected by TLC plate). After cooling to room temperature, the solution is slowly poured into water (200 mL) and the precipitated solid is filtered. Recrystallization from heptane affords 2-(2,6-dimethyl-4H-pyran-4-ylidene) malononitrile in 90% yield. (b) Under argon, 2-(2,6-dimethyl-4H-pyran-4-ylidene) malononitrile (3.44g, 20 mmol) and 4-(dimethylamino)benzaldehyde (1.49g, 10 mmol) are dissolved in dry acetonitrile (100 mL). Piperidine (1.0 ml) is added and the solution is stirred at 40 °C till starting material disappeared (detected by TLC plate). The solution is concentrated and the product is purified by flash column chromatography (elute: petroleum ether / ethyl acetate = 1 / 2, v/v). **1**: Yield: 60%. ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (d, J = 8.8 Hz, 4H), 7.44 (d, J = 16 Hz, 2H), 6.72 (d, J = 12 Hz, 4H), 6.51 (s, 2H), 6.50 (d, J = 16 Hz, 2H), 3.06 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.7, 156.3, 151.2, 137.6, 128.9, 126.0, 124.1, 122.3, 121.9, 115.6,

112.6, 111.2, 104.7, 59.3. HRMS (EI) calcd for C₂₈H₂₆N₄O (M⁺): 434.2107. Found: 434.2108.

(2) **General.** ¹H and ¹³C NMR spectra are recorded at 400 and 100 MHz, respectively, with TMS as an internal reference. MS spectra are recorded with TOC-MS spectrometer, respectively. UV absorption spectra and fluorescence spectra in solution are measured with an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively. Fluorescence quantum yields in solid state are measured in an integrating sphere with a fluorescence spectrophotometer (Edinburgh Instruments FLS-920). All chemicals for synthesis are purchased from commercial suppliers, and solvents are purified according to standard procedures. Reaction is monitored by TLC silica gel plates (60F-254). Column chromatography is performed on silica gel (70-230 mesh).

(3) **Experiment for two-photon absorption and two-photon emission.** The properties of the two photon absorption is studied by femtosecond pulse laser experiment in DCM solution at a concentration of $9.2 \times 10^{-4} \text{ mol L}^{-1}$. The TPA cross section (σ) is determined by the two-photon fluorescence method.² Fluorescein (pH = 11, in water), whose two-photon properties have been well characterized in the literature, is used as reference standard in the measurement. The measurement is conducted in a regime where the fluorescence signal shows a quadratic dependence on the intensity of the excitation beam, as expected for two-photon-induced emission. In two-photon pumped emission experiment, a Ti-sapphire laser system (Mai Tai HP, Spectra-Physics) with a pulse width of 120 fs and a repetition rate of 82 MHz was employed as an excitation light source. The excitation wavelength is from 700 nm to 1050 nm, The energy of excited pulse can be controlled by neutral density filters, and the beam of excite laser was focused into the central of the cuvette with a plan-convex lens (focal length = 100 mm) under experiment. The fluorescence emitted from the sample was collected by a fiber spectrometer (SD 2000, Ocean Optics) and the detect direction is perpendicular to the laser transmission direction.

(4) **Preparation of polymeric thin film containing 1.** PMMA-1 thin film, PS-1 thin film and PBT-1 thin film were prepared as follows: **1** (0.25 mg) was dissolved in 1.0 mL of a PMMA-cyclohexanone solution, a PS-toluene solution and a PBT-dichloromethane solution (10%, w[g]/v[mL]), respectively. A film was obtained by spin coating a 1.0 mL of PMMA-cyclohexanone solution (or 1.0 mL of PS-toluene solution, or 0.1 mL of PBT-DCM solution) on quartz glass (size: 2.5 cm × 1.2 cm), and dried in air at room temperature. The concentration of **1** in PMMA thin film (or PS thin film, or PBT thin film) is ca 0.25%.

References

- (1) Q. Peng, Z. Lu, Y. Huang, M. Xie, S. Han, J. Peng, Y. Cao, *Macromolecules*, 2004, **37**, 260.
- (2) R. R. Tykwinski, U. Gubler, R. E. Martin, F. Diederich, C. Bosshard, P. Günter, *J. Phys. Chem. B*, 1998, **102**, 4451.

2. Photostability

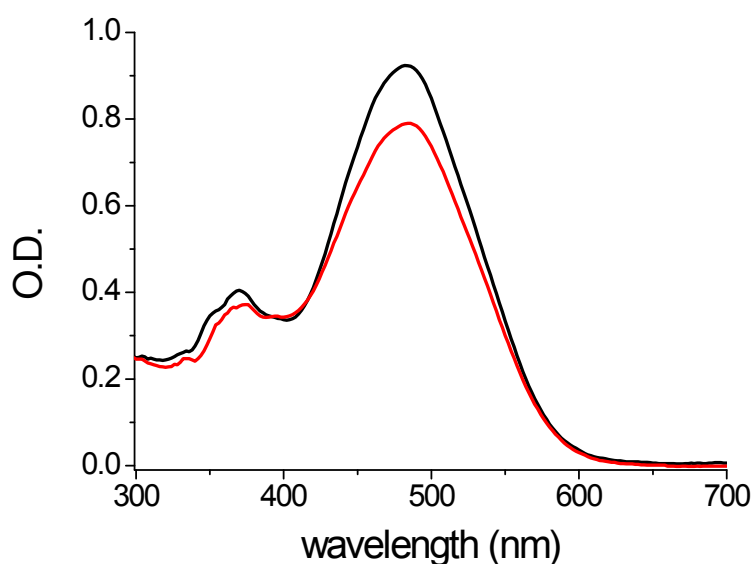


Fig. S1 Absorption spectra of **1**-PMMA thin film before (black) and after (red) UV light irradiation ($\lambda = 365$ nm, $P = 3.7$ mW/cm²) for 60 min.

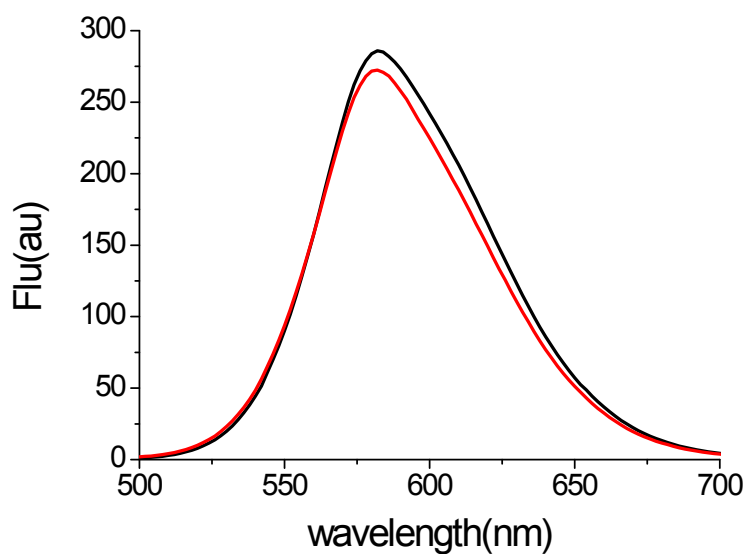


Fig. S2 Fluorescence spectra of **1**-PMMA thin film before (black) and after (red) UV light irradiation ($\lambda = 365$ nm, $P = 3.7$ mW/cm²) for 60 min ($\lambda_{\text{ex}} = 490$ nm).

3. Fluorescence quenching

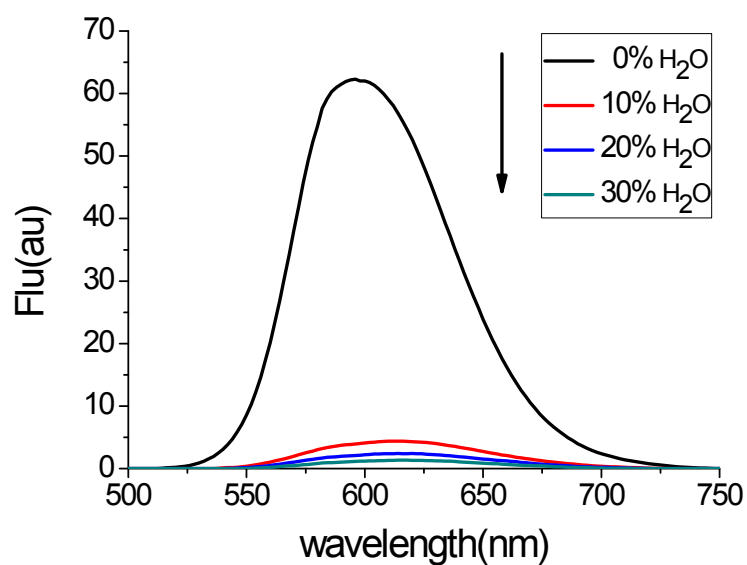


Fig. S3 Fluorescence spectra of **1** (10 μM) in THF-H₂O mixture solution ($\lambda_{\text{ex}} = 490$ nm).