Supplementary Information

Luminescence Emission -Modulated based on specific two-photon compound of triazoleconjugated pyrene derivative

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1. Synthesis of 1,6-di(1-butyl-1H-1,2,3-triazol-4-yl)pyrene (DTP).



Scheme S1 Synthesis of DTP via CuAAC reaction.

The solution of THF (5 mL) and H₂O (2 mL) were added a flask of 58 mg of 1,6diethynylpyrene (0.232 mmol), 92 mg of ^{*n*}BuN₃ (0.93 mmol), 9 mg of CuSO₄·5H₂O (0.036 mmol) and 14 mg of sodium ascorbate (0.071mmol) under N₂ atmosphere. The mixture was heated to 70 °C with vigorous stirring for 12 h. Then the solution was extracted with CH₂Cl₂, and the combined organic phase was dried with anhydrous MgSO₄. After the solvent was removed, the residue was purified by column chromatography on a silica gel using CH₂Cl₂/EtOAc (v/v) 10:1 as eluent. The product was obtained as yellowish solid (50 mg, 48% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, *J* = 5.6 Hz, 2H), 8.25 (m, 4H), 8.13 (d, *J* = 5.6 Hz, 2H), 7.96 (s, 2H), 4.55 (t, *J* = 3.6 Hz, 4H), 2.06 (m, 4H), 1.51 (m, 4H), 1.04 (t, *J* = 5.4 Hz, 6H). EI-MS: m/z calcd for C₂₈H₂₈N₆ 448.2, found 488. EI-HRMS: calcd 448.2375 for C₂₈H₂₈N₆ found 448.2380.

2. Single crystal X-ray diffraction data of DTP

Single crystal of DTP was prepared by slow diffusion of toluene to the THF solution at room temperature. The diffraction experiments were carried out on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data were collected at 173(2) K. Empirical absorption correlations were applied automatically. The structure was solved with direct method and refined with a full-matrix least-squares technique using the SHELXL-97 program. The space group was determined from the systematic absence and its correctness was confined by successful solution and refinement of structure. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms were added in idealized position and refined with isotropic displacement. Crystal data refinement conditions and experimental details were tabulated in Table. S1.



Figure S1 Molecular packing mode in the ac plane of the DTP crystal.

| Identification code | DTP |
|---------------------------------|---------------------------------------------|
| Empirical formula | C28H28N6 |
| Formula weight | 448.56 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 5.4723(11) Å alpha = 95.14(3) deg. |
| | b = 7.4854(15) Å beta = 99.93(3) deg. |
| | c = 15.507(3) Å gamma = 110.92(3) deg. |
| Volume | 576.5(2) Å ^3 |
| Z, Calculated density | 1, 1.292 Mg/m^3 |
| Absorption coefficient | 0.079 mm^-1 |
| F(000) | 238 |
| Crystal size | 0.30 x 0.20 x 0.09 mm |
| Theta range for data collection | 2.70 to 27.48 deg. |
| Limiting indices | -7<=h<=7, -9<=k<=9, -20<=l<=20 |
| Reflections collected / unique | 7497 / 2612 [R(int) = 0.0697] |
| Completeness to theta $= 27.48$ | 99.2 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.0000 and 0.4294 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 2612 / 0 / 155 |
| Goodness-of-fit on F^2 | 1.077 |
| Final R indices [I>2sigma(I)] | R1 = 0.0603, WR2 = 0.1367 |
| R indices (all data) | R1 = 0.0752, $wR2 = 0.1450$ |
| Largest diff. peak and hole | 0.271d -0.225 e. Å ^-3 |

Table. S1 Crystal data and structure refinement for DTP

3. Two-photon-excited fluorescence spectra



Figure. S2 Normalized two-photon-excited fluorescence spectra of DTP in CH_2Cl_2 . The excited wavelength is 740 nm.

4. Representative PL image of DTP nanowires prepared using different anti-solvent.



Figure. S3 Representative PL image of DTP nanowires prepared using different anti-solvent.

(A) toluene; (B) MeOH; (C) EtOH; (D) MeCN.

5. General characterization method of the DTP molecule and DTP nanowires

NMR spectra were recorded in the designated solvent on a Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvent for1H NMR (δ 7.26 ppm for CDCl3). MS data were obtained with a Bruker Daltonics Inc. ApexII FT-ICR mass spectrometer. 1,6-diethynylpyrene1 and n-butyl azide2 were prepared

according to known procedures. UV-Vis spectra were obtained using a TU-1810DSPC spectrometer of Beijing Purkinje General Instrument Co. Ltd. at room temperature in denoted solvents with a conventional 1.0 cm quartz cell.

The DTP nanowires were characterized by SEM (HITACHI S-4300), TEM (Tecnai G2 F20 U-TWIN), and photoluminescence (PL) spectra (HITACHI F-4500). AFM images and cross section profiles were taken on a Bruker Peak Force QNM atom force microscopy. PL images were taken with an Olympus F-1000 inverted micro-scope by exciting the samples with the UV band (330-380 nm) of a mercury lamp. The XRD patterns were obtained using ESCALAB220i-XL X-ray diffraction photometer.

To measure the micro-area PL spectra of single nanowires, the nanowires on a glass substrate were excited with a focused laser (λ =408 nm). The laser was focused down to the diffraction limit to excite the nanowire locally. A confocal microscopy setup was used to selectively collect the emission from the end of the nanowire with a 100 µm pinhole. The excitation laser was filtered with a 400 nm short pass filter. The PL lifetimes of single wires were taken with a Hamamatsu streak camera (C5680, Hamamatsu Photonics).

TPA cross section was determined from two-photon-induced fluorescence with Rhodamine B as a reference. A regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) generated laser pulses of about 120 fs at a wavelength of 795 nm, which were used to drive an optical parameter amplifier (OPA-800CF, Spectra Physics) to obtain a tunable laser in the range of ca. 690–850 nm. The laser beam was focused into a quartz cuvette having an optical path length of 10 mm. The two-photon-induced fluorescence was collected with a right-angle geometry and detected with a liquid-nitrogen-cooled charge coupled device (CCD) detector (SPEC-10-400B/LbN, Roper Scientific) attached to a polychromator (Spectropro-550i, Acton).



Figure. S4 Atomic force microscopy image (A) and the corresponding cross section profile (B) of a single DTP nanowire.



Figure. S5 PL decay profiles of DTP single crystal nanowires at 430 nm under different pumping energies, solution in CH2Cl2 (black circle) and wires (black triangle), respectively. The excitation wavelength is 400 nm. The curve of solution in CH2Cl2 can be fitted by a single exponential function, giving rise to $\tau = 3.85$ ns. The nanowire curves can be fitted by a double-exponential function, giving rise to $\tau 1 = 0.75$ ns (67.9%) and $\tau 2 = 4.02$ ns (22.1%) (raverage = 1.39 ns)

Reference

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