

Supplementary Information

Heating and Mechanical Force-Induced Luminescence on-off Switching of Arylamine Derivative with Highly Distorted Structures

Yujian Zhang,^{a,b} Jingwei Sun,^b Guilin Zhuang,^b Mi Ouyang,^b Zhenwei Yu,^b Feng Cao,^a Guoxiang Pan,^a Peisong Tang,^a Cheng Zhang,^{*b} and Yuguang Ma^{*c}

[a] Dr. Y.J. Zhang, F. Cao, G. X. Pan, P. S. Tang,
Department of Materials chemistry
Huzhou University
Xueshi Road 1#, Huzhou (P. R. China)

[b] Dr. Y.J. Zhang, J. W. Sun, Z. W. Yu, M. Ouyang, G. L. Zhuang, Prof. C. Zhang
College of Chemical Engineering and Materials Science
Zhejiang University of Technology
Chaowang Road 18#, Hangzhou (P. R. China)
E-mail: czhang@zjut.edu.cn

[c] Prof. Y.G. Ma
College of Chemical Engineering and Materials Science State Key
Jinlin University
Qian Jin Road 2699#, Changchun (P. R. China)
E-mail: ygma@jlu.edu.cn

1. Experimental section

Instruments

^1H and ^{13}C NMR spectra of the desired products were recorded on a Bruker AVANCE III 500-MHz instrument (Bruker, Switzerland) using TMS as the internal standard and the chloroform-d (CDCl_3) as the solvent. The UV-vis spectrum was recorded on a Perkin Elmer Lambda 35 spectrophotometer. Fluorescent measurements were recorded on a Perkin-Elmer LS-55 luminescence spectrophotometer. The Φ_f of powder and film was determined by using a calibrated integrating sphere system. Powder XRD measurements were conducted on X'Pert PRO diffractometer ($\text{CuK}\alpha$) in the range $5 < 2\theta < 30$ (PANalytical, Netherlands). X-ray crystallographic intensity data were collected using a Xcalibur, Eos, Gemini Ultra CCD diffractometer equipped with a graphite monochromated Enhance (Mo) X-ray source ($\lambda = 0.71073 \text{ \AA}$). The time-resolved fluorescence lifetime experiments were obtained by time-correlated single photo-counting technique with an Flsp920 spectro-fluorometer. Digital photographs were taken by Canon 550D (Canon, Japan) digital cameras. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC2920 at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$

2 The photophysical properties

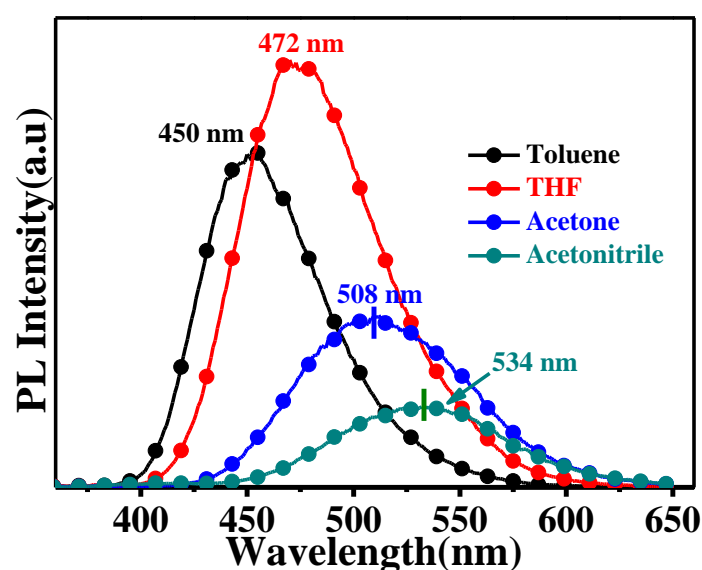


Fig.S1 The emission spectra of solutions of TPA-CO in solvents with different polarities, solution concentration: $10 \mu\text{M}$, solutions were excited at 350 nm

Fig. S1 is the spectra of the compound TPA-CO in effects in organic solvent with various polarities. As the solvent polarity increased from nonpolar toluene to moderately polar THF and to highly polar acetone and acetonitrile (ACN), the emission peaks are gradually red-shifted from 450 nm to 534 nm, exhibiting an obvious bathochromic effect. The fluorescence intensity was also obviously reduced in highly polar media (ACN) relative to THF.

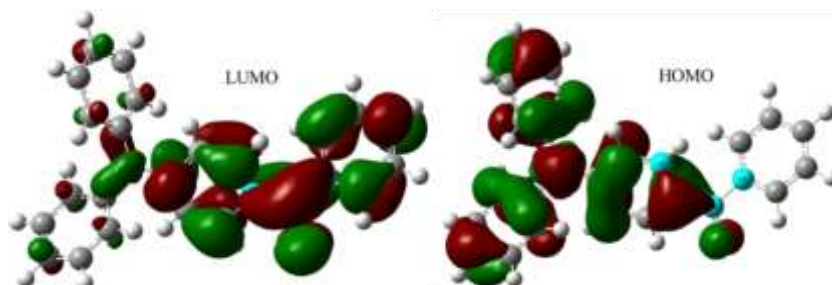


Fig.S2 Pictorial representations of Frontier molecular orbitals calculated at B3LYP/3-21G** for compounds TPA-CO

As shown in **Fig.S2**, the electron clouds of the HOMO levels for compound TPA-CO are mainly located on the electron-donating triphenylamine units; however, those of LUMO levels are dominated by orbitals from the electron-accepting diphenyl ketone peripheries.

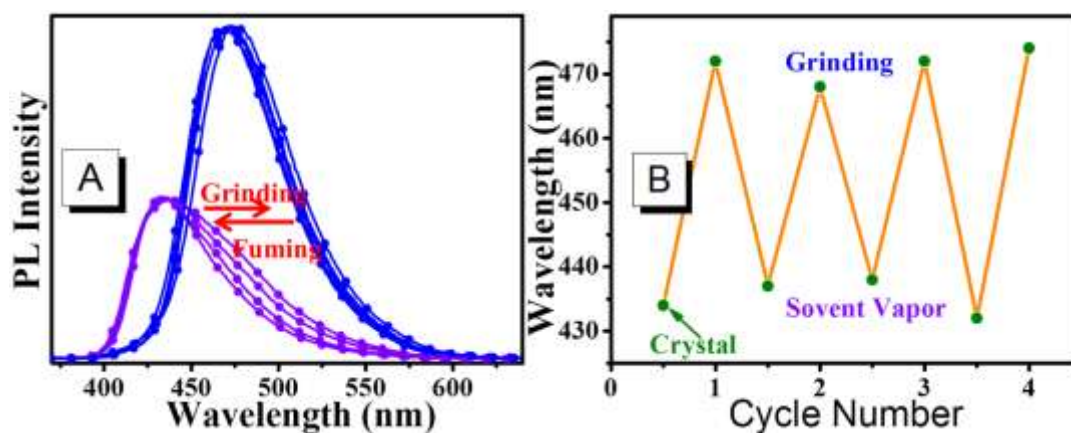


Fig.S3 (A) Change in the PL spectra of TPA-CO by grinding-vapour; (B) Emission wavelength of the repeated stimuli-responsive behaviour by grinding (around 472 nm) and exposing to alcohol (around 436 nm) treatments

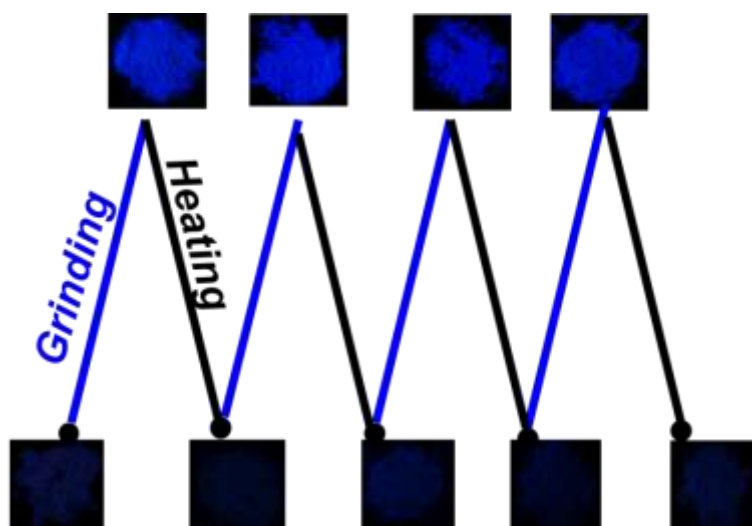


Fig.S4 The switching emission of TPA-CO by repeated grinding-heating processes

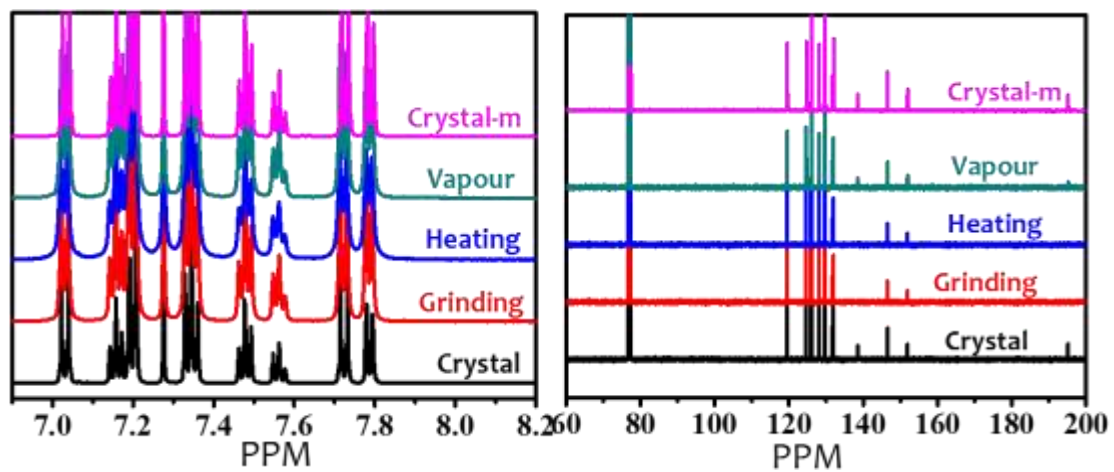


Fig.S5 The NMR of TPA-CO in different states

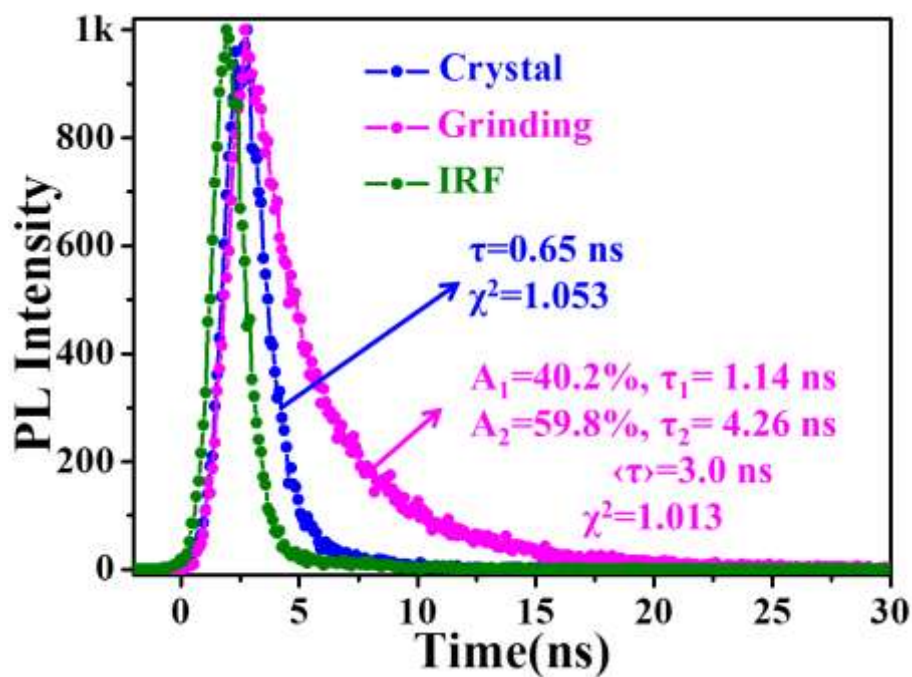


Fig.S6 Fluorescence decay profiles of TPA-CO at different states, excitation wavelength: the absorption and emission peaks

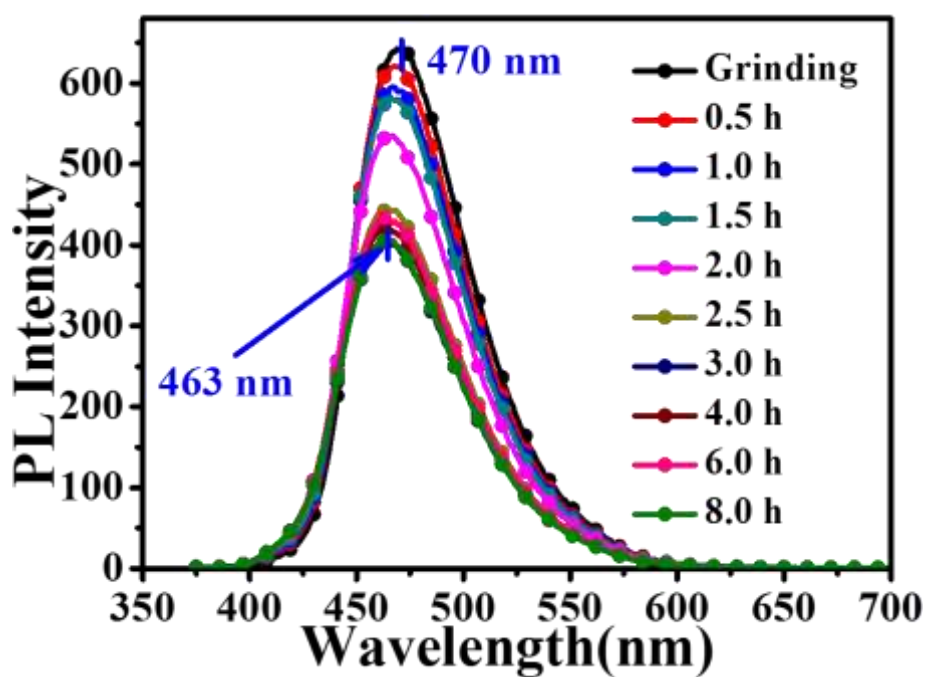


Fig.S7 The change of fluorescence intensity with the time after grinding

3 The Crystal Structures

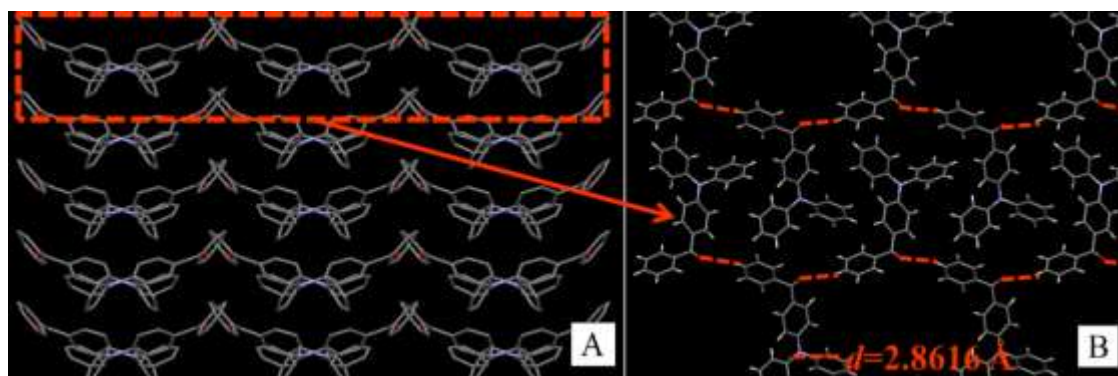


Fig.S8 Molecular stacking structure in the TPA-CO crystal: (A) Side view (B) Top view and illustration of C-H...O

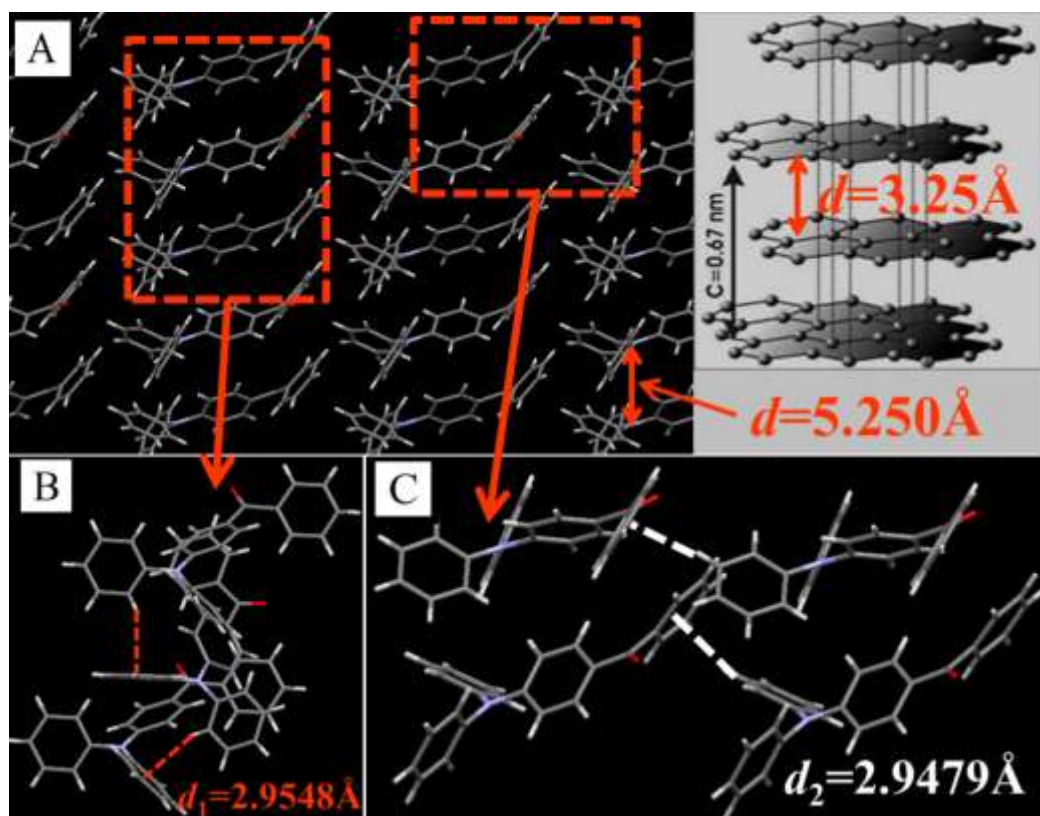


Fig.S9 Two types of C-H... π in the neighbouring sheets (B) and the “molecular sheets”(C)

All of the DFT calculations were performed by using the CASTEP module in Material Studio^[1-3]. The generalized gradient approximation (GGA) with Perdew Burke Ernzerhof (PBE)^[4] was used to describe the exchange-correlation (XC) effects. TS scheme was used for dispersion corrections. This calculation was done with plane wave set using Norm-conserving pseudopotentials^[5] with 750 eV energy cut off. For geometry optimization, the energy tolerance was 2.0×10^{-5} eV per atom with the force tolerance of 0.05 eV/Å, a maximum displacement of 2.0×10^{-3} Å, and a maximum stress tolerance of 0.10 GPa. For self-consistent field (SCF) calculation, the energy tolerance was set to 1.0×10^{-6} eV per atom. According to the structure data of single-crystal diffraction, the initial packing geometry was fully relaxed under external stress of 0.0, 1.0 and 2.0 GPa along *c* axes. In the absence of external stress, the optimized structure is in good agreement with that obtained by single-crystal analysis.

Table S1 optimized lattice parameters under external stress of 0, 1 and 2 GPa along *c* axes

| Stress/GPa | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å | α /° | β /° | γ /° | <i>V</i> /Å ³ |
|------------------|-------------|-------------|-------------|-------------|------------|-------------|--------------------------|
| <i>Exp. Data</i> | 16.740 | 12.432 | 9.236 | 90.0 | 90.0 | 90.0 | 1922.12 |
| 0.0 | 16.910 | 12.470 | 9.078 | 90.0 | 90.0 | 90.0 | 1914.35 |
| 1.0 | 17.505 | 13.023 | 8.195 | 89.9 | 90.2 | 89.9 | 1868.37 |
| 2.0 | 18.26 | 13.46 | 7.59 | 89.7 | 89.6 | 89.5 | 1866.11 |

Table S2 Dihedral angel (Deg^o) θ_1 and θ_2 of molecule **TPA-CO** in optimized unit cell under external stress

| Stress/GPa | θ_1 | θ_2 |
|------------------|------------|------------|
| <i>Exp. Data</i> | 30.50 | 34.02 |
| 0.0 | 30.22 | 36.74 |
| 1.0 | 29.81 | 31.04 |
| 2.0 | 26.28 | 29.64 |

[1] Delley B. *J. Chem. Phys.* 1990, **92** 508

[2] Delley B. *J. Chem. Phys.* 2000, **113** 7756

[3] Delley B. *J. Chem. Phys.* 1991, **94** 7245

[4] Perdew J P, Burke K and Ernzerhof M *Phys. Rev. Lett.* 1996, **77**, 3865.

[5] Bachelet, G. B.; Hamann, D. R.; Schluter, M. *Phys. Rev. B*, 1982, **26**, 4199-4228.