Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Reversible and hydrogen bonding-assisted piezochromic luminescence for solid-state tetraaryl-buta-1,3-diene

Ting Han,[a] Yijia Zhang,[a] Xiao Feng,*[a,b] Zhengguo Lin,[b] Bin Tong,[a] Jianbing Shi,[a] Junge Zhi[b] and Yuping Dong*[a]

[a] *College of Materials Science & Engineering,* [b] *College of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing, 100081, China.*

E-mail: fengxiao86@bit.edu.cn, chdongyp@bit.edu.cn

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Section A. Materials and Methods

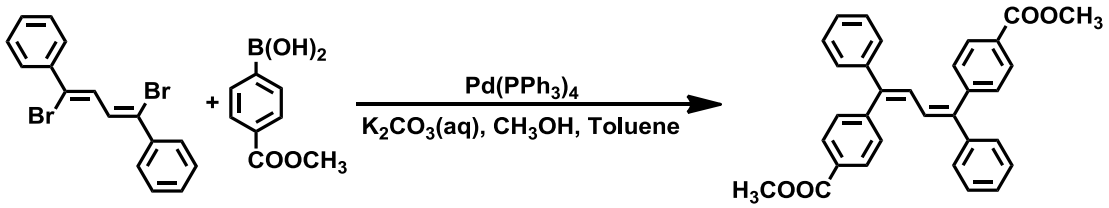
Toluene, methanol and potassium carbonate aqueous solution were degassed prior to use. All other reagents and solvents were used as commercially purchased without further purification. $CuBr_2$ and $PdCl_2$ were purchased from Aladdin and Jiushan Chemical Company, respectively. $Pd(PPh_3)_4$ and phenylacetylene were purchased from J&K Chemical Co..

^{1}H-NMR spectra were recorded on a Varian mercury-plus 400 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on an IRPrestige-21 spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on an Autoflex III MALDI-TOF spectrometer. UV-visible absorption spectra were measured by TU-1901 spectrophotometer. Fluorescence spectra were obtained using a F-7000 fluorescence spectrophotometer. The absolute quantum yield was determined by standard procedure with an integral sphere JASCO model ILF-533 mounted on the FP-6600 spectrofluorometer. Thermal gravimetric analysis (TGA) was performed on a Shimadzu TGA-50 thermal analyzer at a heating rate of 10 ^{o}C/min in nitrogen. Powder X-ray diffraction (PXRD) patterns were analyzed with monochromatized Cu-Kα (λ = 1.54178 Å) incident radiation by a Shimadzu XRD-6000 instrument operating at 40 kV voltage and 50 mA current. Differential scanning calorimetry (thermal analysis, DSC) was performed on a Shimadzu DSC-60 at a heating rate of 10 ^{o}C/min.

Section B. Synthetic Procedures

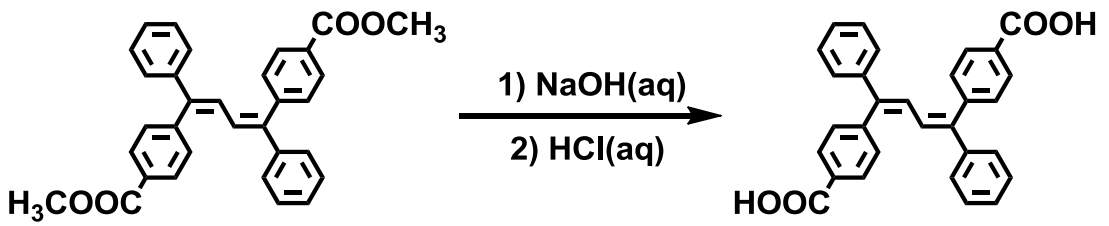
(1*Z*,3*Z*)-1,4-dibromo-1,4-diphenylbuta-1,3-diene (DBDABD) was prepared via the $PdCl_2$-catalyzed dimerization of phenylacetylene according to the references.[1, 2]

Preparation of dimethyl 4,4'-((1*Z*,3*Z*)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzoate (TABD-$COOCH_3$).



DBDABD (1.00 g, 2.75 mmol), 4-methoxycarbonylphenylboronic acid (1.48 g, 8.25 mmol) and $Pd(PPh_3)_4$ (0.32 g, 0.23 mmol) were added to a three-necked flask. Under an atmosphere of argon, the mixed solvents of toluene (60 mL), methanol (20 mL) and potassium carbonate aqueous solution (2.0 mol/L, 16.50 mmol) were added and the mixture was stirred and refluxed for 24 h. After the reaction was finished, the product was extracted with $CHCl_3$ and washed with brine. The organic layer was combined and dried with $MgSO_4$. The crude product was purified by flash column chromatography using dichloromethane/petroleum ether (1:1) as eluent. TABD-$COOCH_3$ was obtained as white solid, yield 95%. IR (KBr): 3029, 2941, 1716, 1275, 1100 cm^{-1}; MALDI-TOF MS: *m*/*z* calcd. 474.55 for $C_{32}H_{26}O_4$, found 474.4; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.40 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.25 (m, 3H, Ar-H), 7.12 (m, 2H, Ar-H), 6.75 (s, 1H, C=C-H), 3.96 (s, 3H, CH_3).

Preparation of 4,4'-((1*Z*,3*Z*)-1,4-diphenylbuta-1,3-diene-1,4-diyl)dibenzoic acid (TABD-COOH).



TABD-$COOCH_3$ (0.77 g, 1.62 mmol) and THF (50 mL) were added to a flask, the mixture was stirred at room temperature until the solid was completely dissolved in THF. Sodium hydroxide aqueous solution (1.25 mol/L, 32.4 mmol) was then added and the mixture was stirred and refluxed for 24 h. After the solution was concentrated under vacuum, HCl diluted solution (3 mol/L) was added dropwise until the pH value was less than 1 as monitored by pH test strips and further stirred for 2 h. After the precipitate was filtered off and washed with water, TABD-COOH was obtained as white solid, yield 98%. IR (KBr) 3432, 3019, 1690, 1422, 1205 cm^{-1}; MALDI-TOF MS: calcd. 446.49 for $C_{30}H_{22}O_4$, found 446.4; ^1H NMR (400 MHz, DMSO) δ = 12.54 (s, 1H, COOH), 8.05 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.42 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.30 (m, 3H, Ar-H), 7.08 (m, 2H, Ar-H), 6.66 (s, 1H, C=C-H).

Section C. TGA Profile

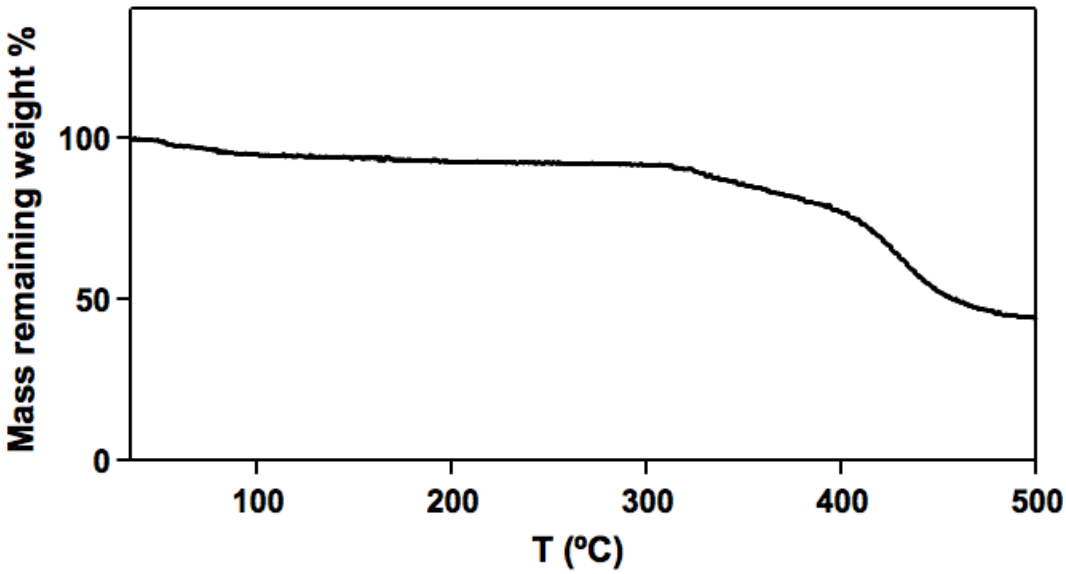


Fig. S1 TGA profile of TABD-COOH.

Section D. Transmission Spectral Profiles

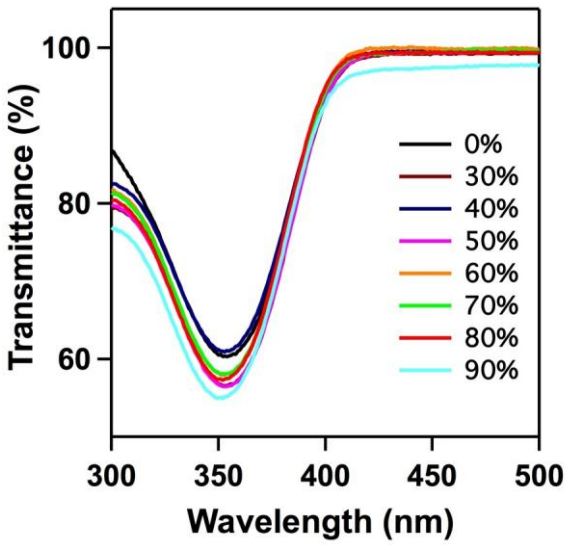


Fig. S2 Transmission spectra of TABD-COOH in THF-hexane mixture with different f_H. TABD-COOH concentration: 10 μM.

Section E. Photographs of Piezochromic Behavior of TABD-COOH

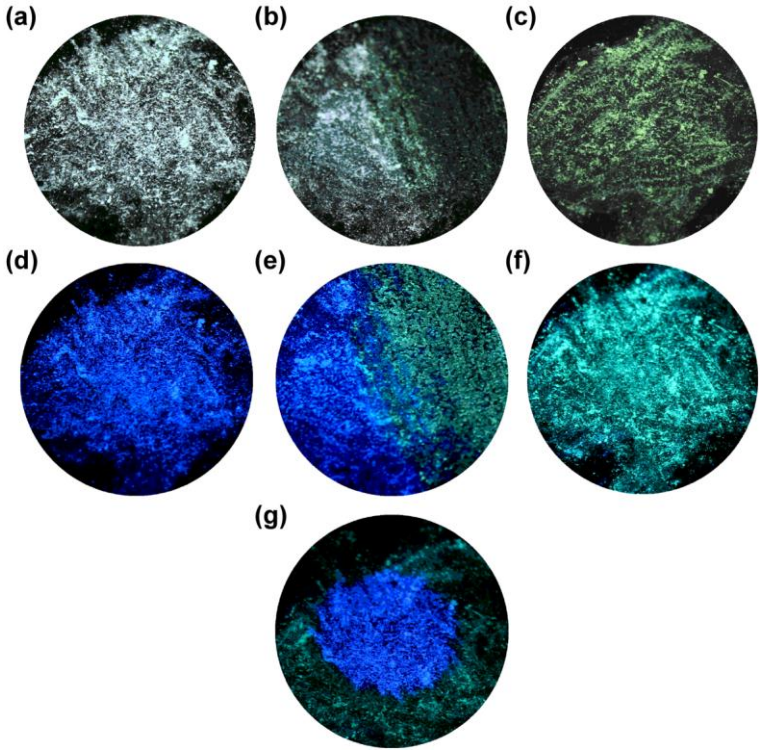


Fig. S3 (a-c) Photographs of a) unground, b) half-ground and c) entire-ground powder of TABD-COOH under ambient light. (e-f) Photographs of corresponding powders under UV irradiation (365 nm). (g) Photograph of entire-ground sample after treatment with a drop of MeOH.

Section F. UV-vis Spectral Profiles

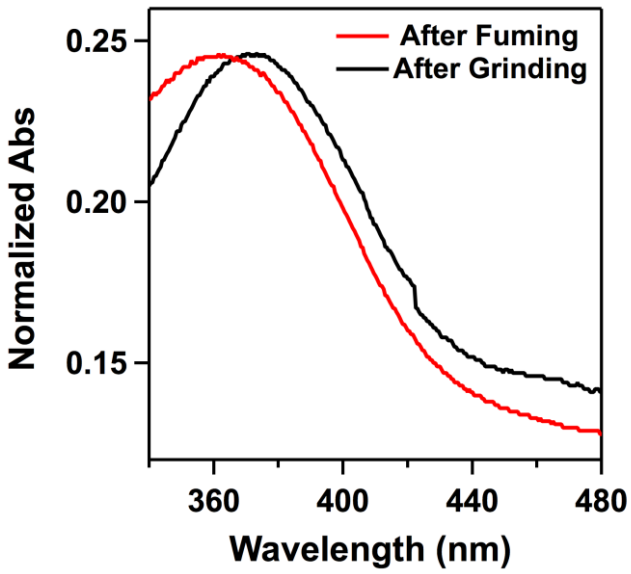


Fig. S4 UV-vis spectra of fumed and ground TABD-COOH.

Section G. FT IR Spectral Profiles

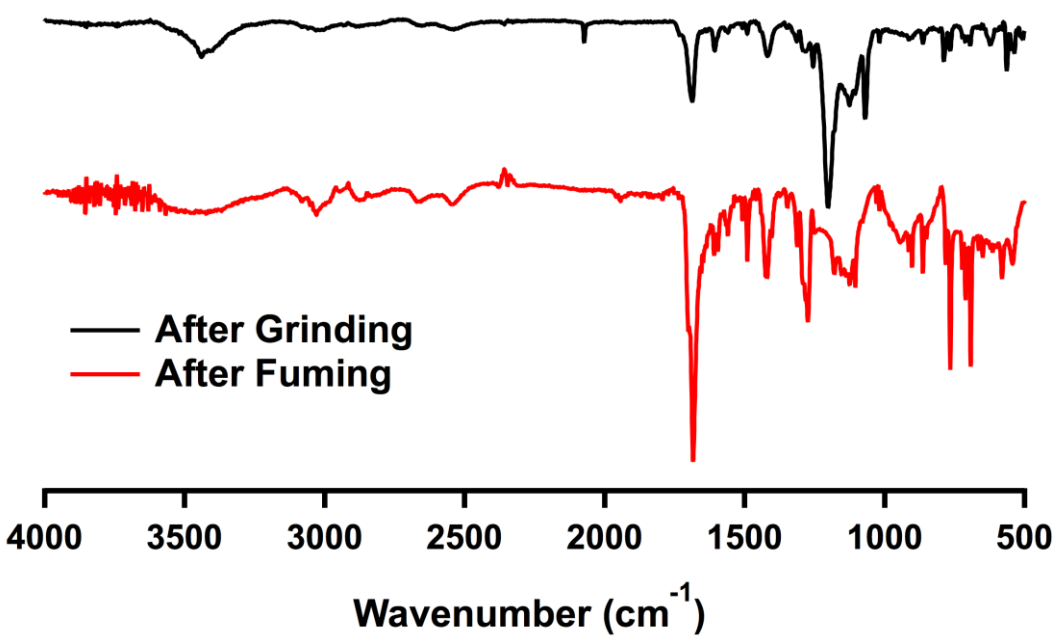


Fig. S5 FT-IR spectra of fumed and ground TABD-COOH.

Section H. PXRD Patterns

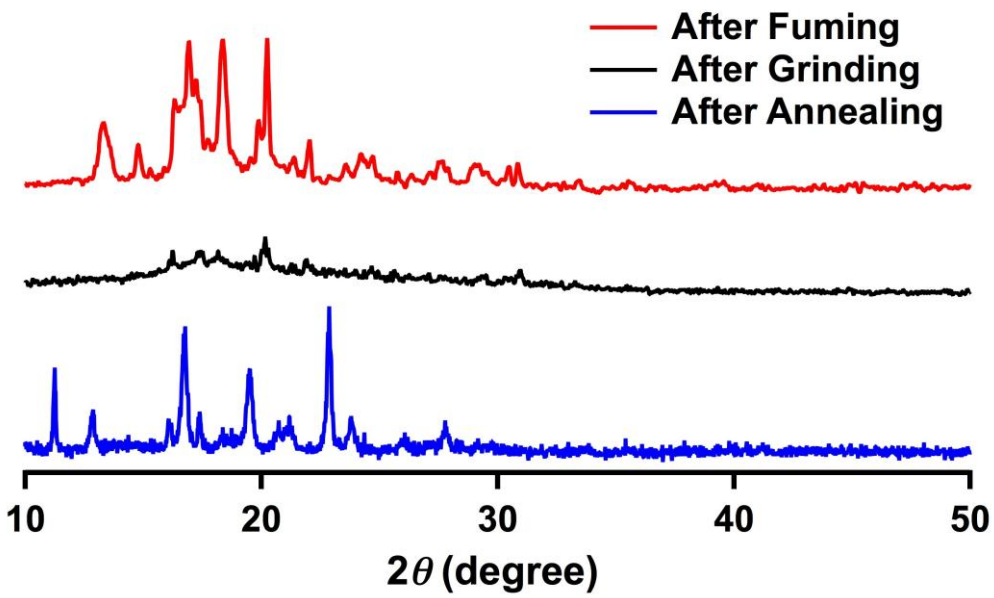


Fig. S6 PXRD patterns of TABD-COOH after fuming, grinding and annealing.

Section I. DSC Profiles

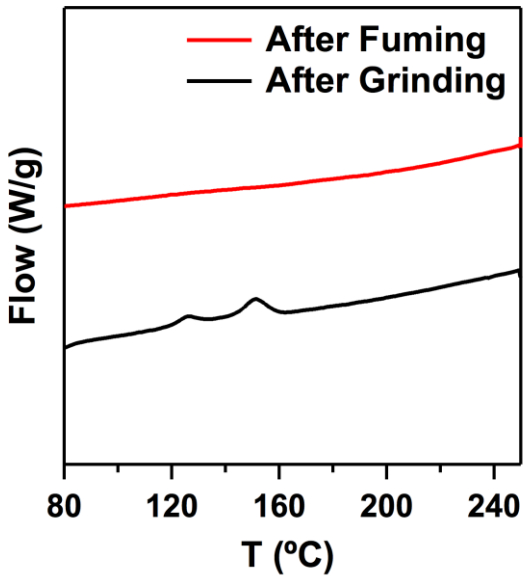


Fig. S7 DSC profiles of fumed and ground TABD-COOH.

Section J. Supporting References

1. J. H. Li, Y. Liang and Y. X. Xie, *J. Org. Chem.*, 2004, **69**, 8125.

2. Y. Liu, X. G. Chen, J. G. Qin, G. Yu and Y. Q. Liu, *Polymer*, 2010, **51**, 3730.