Insight from the Old: Mechanochromism and Mechanoluminescence of Two Amine-containing Tetraphenylethylene Isomers

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Pd(PPh₃)₄, 4-aminophenyl boronic acid, 3-aminophenyl boronic acid, bromotriphenylethylene and other chemicals were all purchased from Energy Chemical Company. K₂CO₃ and solvents were all purchased from Xilong Chemical Co., Ltd.. All the chemicals were used as received without further purification. Compound 4-(1,2,2triphenylvinyl)aniline (p-NH₂) was prepared according to previous paper.¹

Instruments and methods

¹H and ¹³C NMR spectra were recorded on a VNMRS 400 NMR spectrometer (Varian, USA). High resolution mass spectra (HR-MS) were recorded using an Autoflex III mass spectrometer (MALDI-TOF-MS, Bruker, Germany). Element analysis was performed using a vario EL cube elemental analyzer (Elementar, Germany). UV-Vis spectra were recorded using a UV-2600 spectrometer (Shimadzu, Japan). Absolute quantum efficiency was measured on an integrating sphere (C11347-11, Hamamatsu, Japan). The fluorescence quantum yield ($\Phi_{\rm f}$) in solution was measured by a relative method using quinine in 0.1 M H₂SO₄ (Φ_f = 54.6%) as a standard. Fluorescence lifetime was measured on a compact fluorescence lifetime spectrometer (C11367-11, Hamamatsu, Japan). DSC measurements were carried out on a NETZSCH DSC 200F3 instrument at a heating rate and a cooling rate of 10 °C min⁻¹ in nitrogen. TGA analysis was performed on a NETZSCH SA409PC thermogravimeter. Powder X-ray diffraction (PXRD) patterns were carried out in the reflection mode at room temperature using a 2.2 kW Empyrean X-ray Diffraction System (PANalytical, Netherland). The ML spectra were collected from a spectrometer of Acton SP2750 with a liquid-nitrogencooled CCD (SPEC-10, Princeton) as a power detector (data-collection time is 1s and the diameter of optical fiber is 600 µm). The theoretical ground-state geometry and electronic structure of molecule was optimized using the density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31+G(d). All the theoretical calculations were performed using Gaussian 03 package.²

Scheme S1. The synthetic route of *m*-NH₂



Figure S1. The HOMO and LUMO orbital distribution of p-NH₂ and m-NH₂ calculated by B3LYP/6-31+G(d).



Figure S2. The fluorescence spectra of (a) p-NH₂ and (b) m-NH₂ in THF/water mixtures with different water fractions (f_w), concentration: 10 μ M.



Figure S3. Fluorescence decay curves of (a) *p*-NH₂-o, (b) *p*-NH₂-c1 and (c) *p*-NH₂-c2.



Figure S4. Fluorescence decay curves of (a) m-NH₂-o and (b) m-NH₂-c.



Figure S5. Maximum emission wavelength changes of p-NH₂ cast weighing paper versus dichloromethane fuming/grinding cycles.



Figure S6. TG and DTA curves of *p*-NH₂.



Figure S7. TG and DTA curves of *m*-NH₂.



Figure S8. DSC curves of *p*-NH₂-o, *p*-NH₂-g and *p*-NH₂-f.



Figure S9. DSC curves of *m*-NH₂-o, *m*-NH₂-g and *m*-NH₂-f.

	<i>p</i> -NH ₂ -c1	<i>p</i> -NH ₂ -c2	<i>m</i> -NH ₂ -c
CCDC Number	1904509	1904510	1904511
Formula	C26H21N	C26H21N	C26H21N
Formula Weight /g•mol ⁻¹	347.44	347.44	347.44
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P21/c	P21
T/K	291.9	150	293
Ζ	2	8	2
a/Å	9.3883(2)	21.2255(4)	9.8537(5)
b/Å	9.57730(10)	11.3734(2)	9.7409(5)
c/Å	11.6563(2)	17.6183(3)	10.7497(5)
α/o	72.243(2)	90	90
β/0	81.656(2)	113.602(2)	107.104(5)
$\gamma/^{o}$	87.6130(10)	90	90
$V/Å^3$	987.57(3)	3897.38(13)	986.16(9)
ρ _c /g•cm ⁻³	1.168	1.184	1.170
µ/mm⁻¹	0.511	0.518	0.512
F(000)	368	1472	368
Reflections collected	9741	23906	5160
Independent reflections	3860	7673	3222
R _{int}	0.0331	0.0288	0.0183
$R_1(I \geq 2\sigma(I))$	0.0551	0.0614	0.0595
wR_2	0.1544	0.1672	0.1900
GOOF	1.073	1.078	1.082

Table S1. Single crystal data of *p*-NH₂-c1, *p*-NH₂-c2 and *m*-NH₂-c



Figure S10. The unit cell and molecular conformations with labels of carbon/nitrogen atoms and dihedral angles (between the phenyl ring and central ethene group) of (a) p-NH₂-c1, (b) p-NH₂-c2 and (c) m-NH₂-c. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Every amino group in one molecule has two possible positions by virtue of disorder distribution, so the number depicted the occupancy of nitrogen atom.



Figure S11. The detailed intermolecular interactions in crystal (a) p-NH₂-c1, (b and c) p-NH₂-c2 and (d) m-NH₂-c. Bond length of C-H $\cdots \pi$ interaction is the distance between hydrogen atom and the plane of benzene ring.



Figure S12. ¹H NMR of compound *m*-NH₂.



Figure S13. ¹³C NMR of compound *m*-NH₂.



Figure S14. HRMS of compound *m*-NH₂.

References

- 1. M. Luo et al., J. Mol. Eng. Mater. 2013, 1(3), 134007/1-1340007/20.
- 2. Gaussian 03, Revision E.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2009.