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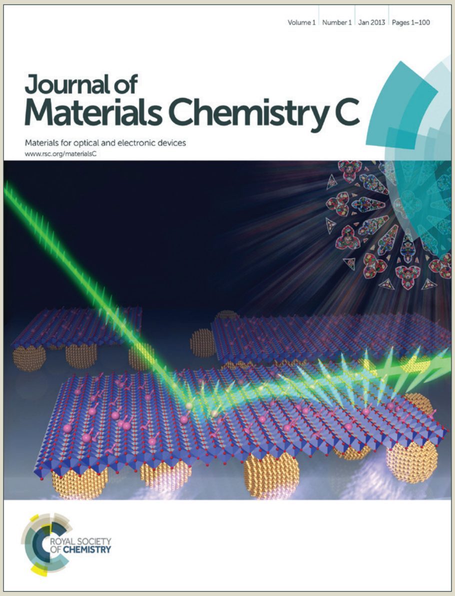

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ARTICLE TYPE

Constitutional isomers of a C_3-symmetric molecule showing different piezochromic behaviours: on-off switching and colour tuning

Yoonbin Lim,[a] Insil Choi,[b] Hyunpyo Lee,[a] Il Won Kim[b] and Ji Young Chang*[a]

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The piezochromic behaviours of C_3-symmetric molecules with *p*-bromophenyl side groups connected to a phenyl ring core through cyano-vinylene bridges were studied. Upon grinding, ***α*-BPAN-Br** having cyano groups at the *α*-position to the phenyl ring core exhibited substantial quenching of a bluish green emission (on-off switching) and its constitutional isomer, ***β*-BPAN-Br** showed an emission colour change from bluish green to deep blue (colour tuning). When the molecules were exposed to an organic vapour, the initial emission of each molecule was restored. The powder X-ray diffraction and DSC studies revealed that the as-synthesized and vapour-annealed samples had the same crystalline structures, while the ground samples had amorphous structures. Their structural analogues, ***α*-BPAN-H** and ***β*-BPAN-H** which had no bromo groups, did not show any piezochromic or vapochromic behaviour. **Poly(*β*-BPAN)** consisting of covalently linked *β*-BPAN units were prepared by Ullmann reaction of ***β*-BPAN-Br**. The polymer showed similar luminescence to that of crystalline ***β*-BPAN-Br**, but its initial emission was not changed by grinding.

Introduction

Luminescent materials are of great interest because of their potential applications such as in displays,[1,2] sensors,[3] and memory devices.[4] In recent years, considerable efforts have been made to control the luminescence properties with external stimuli such as temperature,[5-8] light,[8-10] vapour,[11-14] or pH.[14,15] Mechanical stress is one of the simplest stimuli that can be applied to a responsive material. Piezochormic materials, showing reversible and repeatable colour change induced by mechanical stress, are being widely studied in this context.[5-7,11-26] In recent years, various piezochromic materials with different luminophores such as anthracene,[5] diphenyldibenzofulvene,[19] cyanostyrylbenzene,[12] pyrene,[15,26] tetraphenylethene,[22] and triphenylamine have been investigated.[23,24]

Piezochromic materials exhibiting significant change in their luminescence intensities by mechanical shearing are particularly attractive because they can be utilized for on-off switching of digital signals. A few examples for on-off switchable piezochromic materials have been reported.[18-20] Tang's research group demonstrated the reversible switching of emission intensities of piezochromic materials based on diphenyldibenzofulvenes.[19] Luo *et al.* used a donor–acceptor system for on-off switching. The fluorescence of the co-crystallised complex between 2,5-di(*E*)-distyrylfuran as an electron donor and an *N*-alkyl substituted maleimide as an acceptor was quenched when deposited on the substrate but recovered by applying mechanical force.[20] Kwon *et al.* achieved an on-off switching with a donor–acceptor–donor triad molecule containing dicyanodistyrylbenzene and carbazole moieties.[18]

In this work, four types of C_3-symmetric molecules having cyano-vinylene bridges and a phenyl ring core were synthesized (Scheme 1) and their structural effects on the piezochromism were investigated. ***α*-BPAN-H** and ***α*-BPAN-Br** have cyano groups at the *α*-position to the phenyl ring core and ***β*-BPAN-H** and ***β*-BPAN-Br** have cyano groups at the *β*-position to the core. A network polymer was also prepared by Ullmann reaction of ***β*-BPAN-Br** to compare its optical properties with those of ***β*-BPAN-Br**.

Experimental

Materials

Benzene-1,3,5-tricarbaldehyde[27] and (benzene-1,3,5-triyl)triacetonitrile[28] were prepared according to the literatures. All other chemicals were purchased from Aldrich or Tokyo Chemical Industry and used without any further purification.

Measurements

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 300 spectrometer (300 MHz). ^{13}C NMR spectra were recorded on a Jeol JNM-LA400 (100 MHz). Solid-state ^{13}C NMR spectra were recorded on a BrukerAvance 400WB spectrometer (100 MHz) equipped with a CP-MAS probe. Elemental analyses were performed using a Flash EA 1112 elemental analyzer. Differential scanning calorimetry (DSC) measurements were made on a TA modulated DSC Q10 with a scanning rate of 10 °C/min under nitrogen. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker New D8 Advance (Cu Kα radiation, λ = 1.54 Å). UV-Vis spectra were obtained using a Sinco S-3150 spectrometer. Photoluminescence (PL) measurements were performed on a Shimadzu RF-5301PC spectrofluorometer. The FT-IR spectra were measured with a Thermo Scientific Nicolet 6700 FT-IR spectrometer using KBr pellets. N_2 uptake amounts were measured using a Belsorp-Max (BEL Japan, Inc.) apparatus.

Crystal structure prediction

The packing propensity of the ***α*-BPAN-Br** and ***β*-BPAN-Br** was investigated through crystal structure prediction using the Polymorph Predictor module of the Materials Studio software package (version 6.1, 2012; Accelrys). The molecular structures of two molecules were drawn, and their structures were individually optimized through the energy minimisation in the COMPASS force field.[29] The resulting structures were used as the input for the Polymorph Predictor.[30,31] The Polymorph Predictor was performed in the COMPASS force field with integral charges, and the calculation of the van der Waals and Coulomb interactions was done through the Ewald summation method.[32] No rigid body constraints were applied during the process. The process of the Monte Carlo simulated annealing (100,000 K to 300 K) was independently repeated 26 times for each molecule to obtain reproducible results. The number of the trial structures for each run was set as 7,000, and the number of the final structures per run was between 24 and 159 after clustering. The explored space group was limited to the P2/m based on the indexing of the powder XRD patterns through GSAS-II utilizing the index algorithm by singular value decomposition.[33-35] The predicted structures were ranked according to the lattice energy, and only the structures of the lowest energy per each run were compared (total 26). Finally, the multiple repeated structures were extracted as the final results.

(Benzene-1,3,5-triyl)tris(3-phenylacrylonitrile) (*α*-BPAN-H)

To a solution of (benzene-1,3,5-triyl)triacetonitrile (0.100 g, 0.512 mmol) and benzaldehyde (0.169 g, 1.59 mmol) in ethanol (30 mL) and tetrahydrofuran (THF, 3 mL) was added sodium hydroxide (0.123 g, 3.07 mmol) in ethanol (10 mL). After stirring for 12 h at room temperature, the precipitate was filtered and washed with ethanol. The product was obtained as a yellow solid. Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.977 (m, Ar-H, 6H), δ 7.957 (s, Ar-H, 3H), δ 7.696 (s, vinyl, 3H), δ 7.521 (m, Ar-H, 9H). ^{13}C NMR (400 MHz, DMSO-d^6, ppm): δ 145.32, 135.83, 133.44, 131.13, 129.35, 129.07, 123.86, 117.59, 109.11. Elemental Analysis: Calc. for $C_{33}H_{21}N_3$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.30; H, 4.45; N, 9.04.

(Benzene-1,3,5-triyl)tris(3-(4-bromophenyl)acrylonitrile) (*α*-BPAN-Br)

To a solution of (benzene-1,3,5-triyl)triacetonitrile (0.300 g, 1.54 mmol) and 4-bromobenzaldehyde (0.506 g, 4.76 mmol) in ethanol (50 mL) and THF (6 mL) was added sodium hydroxide (0.369 g, 9.22 mmol) in ethanol (20 mL). After stirring for 12 h at room temperature, the precipitate was filtered and washed with ethanol. The product was obtained as a pale yellow solid. Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.936 (s, Ar-H, 3H), δ 7.837 (d, J = 8.7Hz, Ar-H, 6H), δ 7.670 (d, J = 8.7Hz, Ar-H, 6H), δ 7.612 (s, vinyl, 3H). ^{13}C NMR (400 MHz, THF-d^8, ppm): δ 144.00, 137.76, 133.98, 133.29, 132.12, 126.14, 125.36, 118.00, 111.91. Elemental Analysis: Calc. for $C_{33}H_{18}Br_3N_3$: C, 56.93; H, 2.61; N, 6.04. Found: C, 57.02; H, 2.60; N, 6.10.

(Benzene-1,3,5-triyl)tris(2-phenylacrylonitrile) (*β*-BPAN-H)

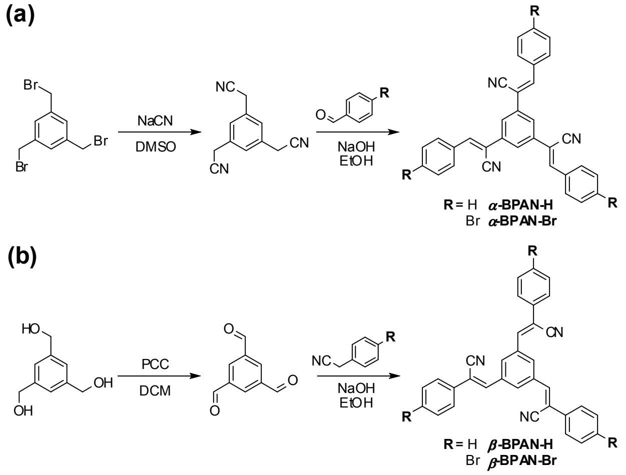
To a solution of benzene-1,3,5-tricarbaldehyde (0.100 g, 0.617 mmol) and phenylacetonitrile (0.224 g, 1.91 mmol) in ethanol (30 mL) and THF (3 mL) was added sodium hydroxide (0.148 g, 3.70 mmol) in ethanol (10 mL). After stirring for 12 h at room temperature, the precipitate was filtered and washed with ethanol. The product was obtained as a pale yellow solid. Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.443 (s, Ar-H, 3H), 7.764 (m, Ar-H, 6H), 7.738 (s, vinyl, 3H), 7.518 (m, Ar-H, 9H). ^{13}C NMR (400 MHz, DMSO-d^6, ppm): δ 141.38, 135.21, 133.18, 130.54, 129.82, 129.34, 126.04, 117.19, 112.95. Elemental Analysis: Calc. for $C_{33}H_{21}N_3$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.27; H, 4.57; N, 9.09.

(Benzene-1,3,5-triyl)tris(2-(4-bromophenyl)acrylonitrile) (*β*-BPAN-Br)

To a solution of benzene-1,3,5-tricarbaldehyde (0.100 g, 0.617 mmol) and 4-bromophenylacetonitrile (0.375 g, 1.91 mmol) in ethanol (30 mL) and THF (3 mL) was added sodium hydroxide (0.148 g, 3.70 mmol) in ethanol (10 mL). After stirring for 12 h at room temperature, the precipitate was filtered and washed with ethanol. The product was obtained as a pale yellow solid. Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.396 (s, Ar-H, 3H), 7.645 (d, J = 9.0Hz, Ar-H, 6H), 7.604 (d, J = 9.0Hz, Ar-H, 6H), 7.852 (s, vinyl, 3H). ^{13}C NMR (400 MHz, DMSO-d^6, ppm): δ 141.93, 135.14, 132.44, 132.26, 130.74, 128.07, 123.20, 116.85, 111.94. Elemental Analysis: Calc. for $C_{33}H_{18}Br_3N_3$: C, 56.93; H, 2.61; N, 6.04. Found: C, 56.67; H, 2.67; N, 6.02.

Results and discussion

C$_3$-symmetric molecules having cyano-vinylene bridges and a phenyl ring core were synthesized via Knoevenagel condensation reaction as shown in Scheme 1.[36] For **α-BPAN-H** and **α-BPAN-Br**, (benzene-1,3,5-triyl)triacetonitrile was reacted with benzaldehyde and 4-bromobenzaldehyde, respectively, in ethanol in the presence of sodium hydroxide. In the case of **β-BPAN-H** and **β-BPAN-Br**, benzene-1,3,5-tricarbaldehyde was reacted with phenylacetonitrile and 4-bromophenylacetonitrile, respectively. The compounds obtained were bright yellow solids and characterized by ^{1}H NMR, ^{13}C NMR and element analysis.



Scheme 1 Synthesis of (a) **α-BPAN-H** and **α-BPAN-Br** and (b) **β-BPAN-H** and **β-BPAN-Br**.

α-BPAN-Br and **β-BPAN-Br** showed no significant difference in the band gap, showing almost the same absorption spectra in THF (5.0×10^{-5} M) with the absorption onset around 375 nm (Fig. 1a); however, their emission behaviours significantly differed when excited at 365 nm. While no noticeable emission was observed from **α-BPAN-Br** in THF, an intense blue emission with a peak maximum at 415 nm was detected from **β-BPAN-Br** in THF (Fig. 1b). **α-BPAN-H** and **β-BPAN-H** showed the absorption maxima at 318 and 324 nm, respectively in THF (5.0×10^{-5} M) (Fig. 1c). **α-BPAN-H** exhibited a weak blue emission with peak maximum at 412, while **β-BPAN-H** showed a strong blue emission with peak maximum at 427 nm when excited at 365 nm (Fig. 1d).

In the solid states, the compounds showed different emission properties from those in the solution states where they are considered to exist as monomers.[12] When excited at 365 nm, both the **α-BPAN-Br** and **β-BPAN-Br** compounds exhibited bluish green luminescence with a peak maximum at 493 nm and at 483 nm, respectively (Fig. 2). **α-BPAN-H** and **β-BPAN-H** showed blue emissions with peak maxima at 455 and 437 nm, respectively (Fig. 3).

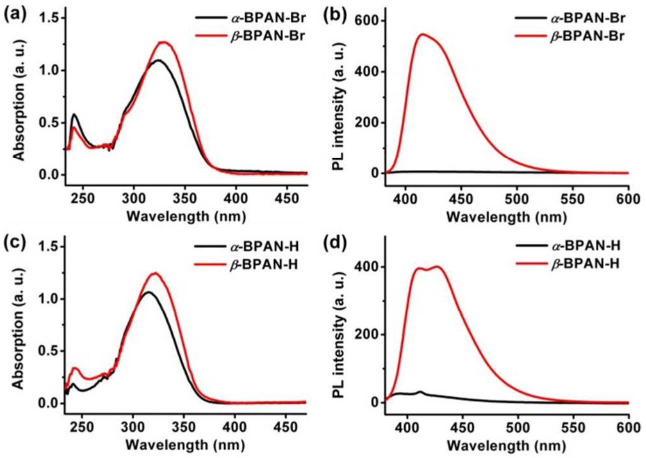


Fig. 1 (a) Absorption and (b) PL spectra of **α-BPAN-Br** and **β-BPAN-Br** in THF (5.0×10^{-5} M) (λ_{ex} = 365 nm). (c) Absorption and (d) PL spectra of **α-BPAN-H** and **β-BPAN-H** in THF (5.0×10^{-5} M) (λ_{ex} = 365 nm).

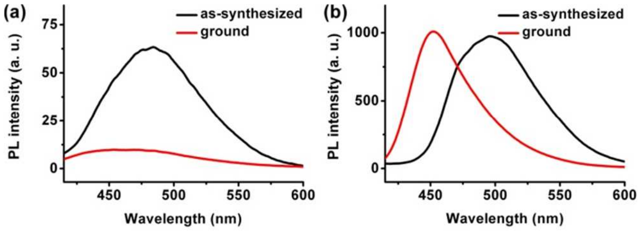


Fig. 2 PL spectra of (a) **α-BPAN-Br** and (b) **β-BPAN-Br** measured in as-synthesized and ground states (λ_{ex} = 365 nm).

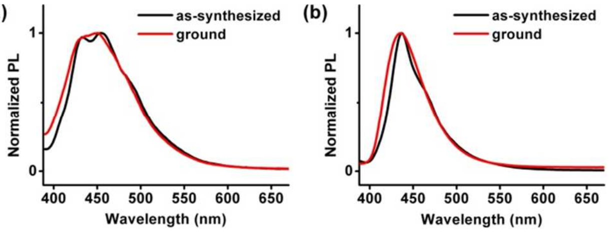


Fig. 3 PL spectra of (a) **α-BPAN-H** and (b) **β-BPAN-H** measured in as-synthesized and ground states (λ_{ex} = 365 nm).

It is worth noting that only the compounds bearing bromo groups displayed piezochromiosm. Upon grinding, **α-BPAN-Br** and **β-BPAN-Br** changed from opaque bright yellow solids to colourless solids and their luminescence colour changed considerably, while the colour and luminescence of **α-BPAN-H** and **β-BPAN-H** showed no significant change. More interestingly, the two constitutional isomers, **α-BPAN-Br** and **β-BPAN-Br**, showed very different piezochromic properties. When the ground samples were excited at 365 nm, **β-BPAN-Br** showed a blue emission with a peak maximum at 368 nm, which was 47 nm blue-shifted, while the luminescence of **α-BPAN-Br** was almost quenched. The emission patterns of **α-BPAN-Br** and **β-BPAN-Br** observed in the ground state were similar to those observed in the monomer state.

When the ground samples of **α-BPAN-Br** and **β-BPAN-Br** were exposed to the vapours of organic solvents, their initial luminescence colours were restored. Although common organic solvents such as THF, ethyl acetate (EA), acetone, chloroform and dichloromethane were useful for the luminescence restoration, EA and THF were the most effective for **α-BPAN-Br** and **β-BPAN-Br**, respectively. The original bright yellow colour appeared within one minute when the ground compounds were in contact with the vapour of EA or THF. Upon excitation at 365 nm, they showed bluish green luminescence as observed in the as-synthesized compounds (Fig. 4). The restoration of the luminescence as well as the solid colour suggested that the organic solvent vapour provided sufficient driving force for the rearrangement of the molecules into the ordered phase.

As a demonstration for practical applications of these piezochromic and vapochromic properties of **α-BPAN-Br** and **β-BPAN-Br**, we attempted piezochromic writing and vapochromic erasing.[20,25] Two non-fluorescent filter papers were wetted with solutions of **α-BPAN-Br** and **β-BPAN-Br** in EA and THF, respectively.[13,25] As the solvents had evaporated, the filter papers emitted bluish green luminescence similar to the as-synthesized compounds. When the letters 'SNU' were written on the papers with a rod, distinct changes in the luminescence were observed only at the regions where mechanical forces were applied (Fig. 5). The letters written on the paper of **α-BPAN-Br** appeared dark while those of **β-BPAN-Br** showed blue emission. When the letters on the **α-BPAN-Br** and **β-BPAN-Br** solution-wetted papers were exposed to EA and THF vapour, respectively, they were erased as the initial luminescences were recovered. These piezochromic writing and vapochromic erasing behaviours agreed well with the piezochromic and vapochromic properties of the solid compounds as shown in Fig. 4.

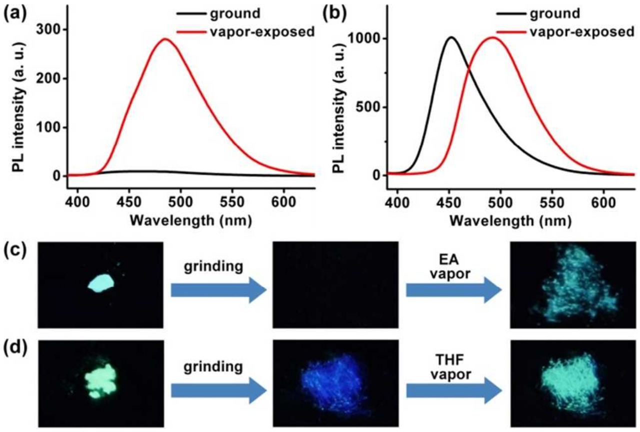


Fig. 4 PL spectra of the ground samples, (a) **α-BPAN-Br** and (b) **β-BPAN-Br** measured after vapor-exposure (λ_{ex} = 365 nm). PL changes of (c) **α-BPAN-Br** and (d) **β-BPAN-Br** by grinding and vapor exposure (λ_{ex} = 365 nm).

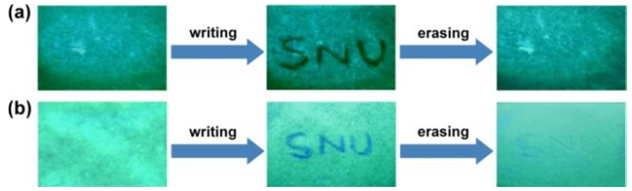


Fig. 5 Piezochromic writing and vapochromic erasing of the letters 'SNU' written on filter papers wetted with solutions of (a) **α-BPAN-Br** and (b) **β-BPAN-Br** in EA and THF, respectively.

It has been proposed that piezochromism occurs by destruction of an ordered structure by external mechanical forces although its definite mechanism is still under controversy.[16] The idea that macroscopic mechanical forces substantially alter the microscopic nanostructure seemed to be acceptable at least based on PXRD and DSC analysis results for **α-BPAN-Br** and **β-BPAN-Br**.[11,15,18] The as-synthesized samples of **α-BPAN-Br** and **β-BPAN-Br** exhibited crystalline PXRD patterns with sharp and strong peaks. When these compounds were ground, they showed no noticeable peaks, indicating the transition from the crystalline states to amorphous states (Fig. 6). The crystalline peaks appeared again after exposure of the ground samples to the EA or THF vapour, suggesting the restoration of their initial phases. The crystallisation by the solvent vapour treatment was also confirmed by DSC.[11,26] As-synthesized **α-BPAN-Br** and **β-BPAN-Br** showed melt transitions near 210 °C and 240 °C, respectively in the first heating scan. In contrast, the ground samples of **α-BPAN-Br** and **β-BPAN-Br** showed exothermic crystallisation peaks at 98 °C and 109 °C, respectively, followed by melt transition peaks (Fig. 7). The ground sample of **α-BPAN-Br** showed a very small crystallisation peak, indicating slow crystallisation. The lower crystallisability of **α-BPAN-Br** compared to **β-BPAN-Br** could be associated with the steric effect of the *α*-nitrile groups on the conformation of the molecule. The crystallisation peaks did not appear in the DSC thermograms of the vapour-annealed samples. These results were consistent with the PXRD results in which the ordered crystalline phases of **α-BPAN-Br** and **β-BPAN-Br** were changed to the amorphous phases by grinding and were restored by the solvent vapour exposure.[11,18]

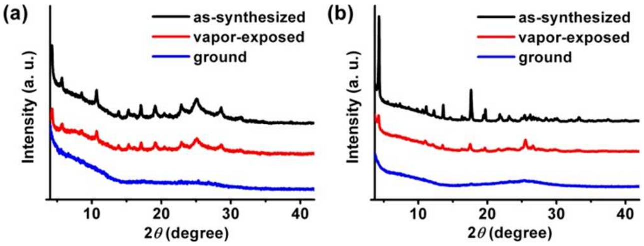


Fig. 6 PXRD patterns of (a) **α-BPAN-Br** and (b) **β-BPAN-Br**.

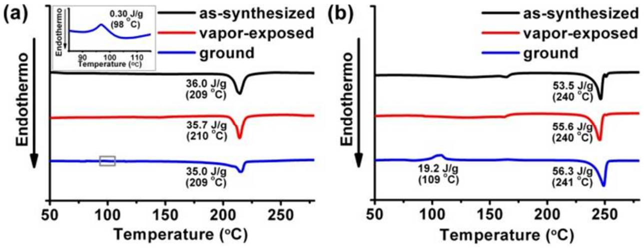


Fig. 7 DSC curves of (a) **α-BPAN-Br** (inset: a magnified curve of the ground sample) and (b) **β-BPAN-Br**.

A considerable difference in the piezochromic behaviours of the two constitutional isomers, **α-BPAN-Br** and **β-BPAN-Br**, were also of significant interest. To elucidate the origin of this discrepancy, we attempted to grow crystals with single crystal X-ray diffraction qualities, but failed to obtain good crystals probably due to the three-branched complicated structures of the two molecules. Instead, crystal structure prediction using the Polymorph Predictor module of the Materials Studio was adopted for the investigation of crystal structures of each molecule.[30,31] The optimized structures with minimum lattice energy were obtained with systematic calculation of van der Waals and Coulomb interactions, as explained in detail in the experimental section. As a result, a striking contrast was observed between the optimized structures of ***α*-BPAN-Br** and ***β*-BPAN-Br**. While ***α*-BPAN-Br** has twisted conformations between the phenyl ring core and branches, ***β*-BPAN-Br** has a perfectly planar structure over the entire molecule (Fig. 8). This difference in molecular structures in crystalline states is ascribed to the different positions and steric effects of the nitrile groups in each molecule. In ***α*-BPAN-Br**, three nitrile groups are located at the *α*-positions to the phenyl ring core, making the molecular centre more crowded than in the case of ***β*-BPAN-Br**. This crowdedness causes higher conformational torsion for ***α*-BPAN-Br** relative to ***β*-BPAN-Br**, promoting molecular motions.[37] Luminescence quenching of ***α*-BPAN-Br** in the monomer and ground states is likely because the excited energy was mostly lost by non-radiative pathways such as vibrational and rotational motions.[12] On the other hand, the perfectly planar structure of ***β*-BPAN-Br** in crystalline state suppresses molecular motions, and the excited energies are consumed in the form of luminescence. With this relationship between molecular structures and piezochromic behaviours observed in ***α*-BPAN-Br** and ***β*-BPAN-Br**, we found that it is possible to modulate on-off switching and colour tuning by changing the position of bulky groups.

To further understand the role of the weak intermolecular bondings for piezochromism, we prepared a polymer, **Poly(*β*-BPAN)**, by Ullmann reaction of ***β*-BPAN-Br**.[38] **Poly(*β*-BPAN)** consisted of *β*-BPAN units, which were linked covalently to each other. The polymer structure was characterized by solid-state ^{13}C NMR and FT-IR spectroscopy (Fig. 9). In the solid-state ^{13}C NMR spectrum, the carbon peaks for the cyano groups and phenyl groups appeared at 115 and 119-136 ppm, respectively. The FT-IR spectroscopy showed that a characteristic absorption band for a carbon-bromine bond at 488 cm^{-1} disappeared after polymerisation.[38] The polymer was isolated as yellow powders. Since ***β*-BPAN-Br** had three reactive sites, **Poly(*β*-BPAN)** had a network structure. The Brunauer–Emmett–Teller (BET) surface area of the polymer calculated from the N$_2$ adsorption isotherm at 77 K was 42.5 m^{2}g^{-1} (Fig. 10a).

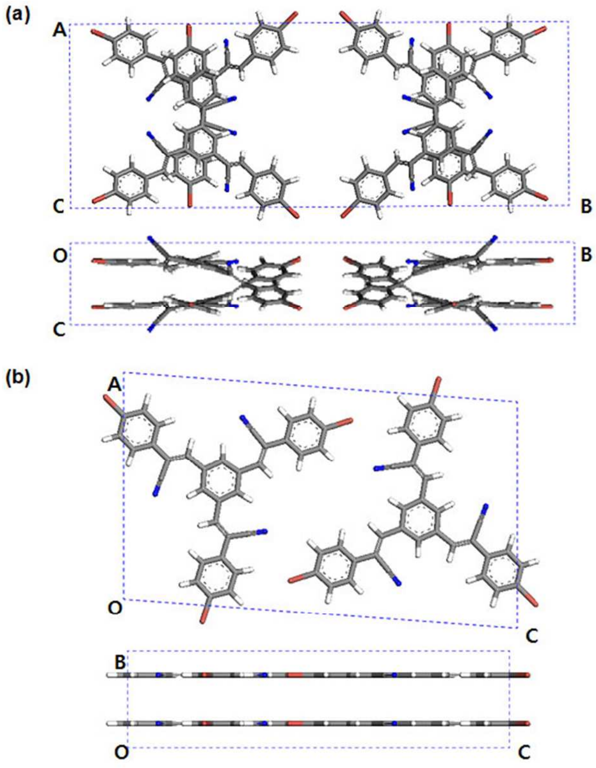


Fig. 8 Optimized structures of (a) ***α*-BPAN-Br** and (b) ***β*-BPAN-Br** calculated with Polymorph Predictor in Materials Studio 6.1.

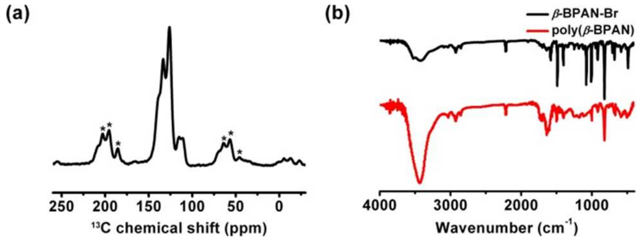


Fig. 9 (a) Solid-state ^{13}C NMR spectrum of **Poly(*β*-BPAN)** and (b) FT-IR spectra of ***β*-BPAN-Br** and **Poly(*β*-BPAN)**.

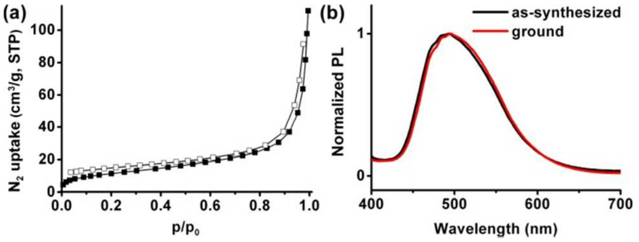


Fig. 10 (a) Nitrogen sorption isotherm curves of **Poly(*β*-BPAN-Br)** and (b) PL spectra of as-synthesized and ground **Poly(*β*-BPAN-Br)**.

The polymer showed blue luminescence at 365 nm excitation as crystalline ***β*-BPAN-Br**. However, its initial emission was not changed by grinding (Fig. 10b), which was a completely different behaviour compared with the crystalline monomer. Apparently, the external mechanical force could not alter the covalently linked network structure of **Poly(*β*-BPAN)**.

Conclusions

We prepared four types of conjugated C_3-symmetric molecules with a phenyl ring core and investigated their piezochromism. Among them, two constitutional isomers ***α*-BPAN-Br** and ***β*-BPAN-Br**, having bromine atoms at the branched phenyl groups showed piezochromism. Upon grinding, ***α*-BPAN-Br** exhibited substantial quenching of a bluish green emission while ***β*-BPAN-Br** showed luminescence colour change from bluish green to deep blue. This discrepancy was ascribed to the difference of crowdedness in the vicinities of cores, which caused different degree of molecular torsion. The initial emission of each molecule was restored by exposure to an organic solvent vapour. PXRD and DSC studies revealed that the piezochromic and vapochromic behaviours were operated by the destruction and reconstruction of the ordered structures of the compounds. Their structural analogues, ***α*-BPAN-H** and ***β*-BPAN-H**, which had no bromo groups, however, did not show any piezochromic or vapochromicbehavior. **Poly(*β*-BPAN)**, comprised of covalently linked *β*-BPAN units, also did not show any piezochromic or vapochromicbehavior. These results led to the conclusion that the transitions between ordered and disordered phases by external stimuli were enabled due to the weak intermolecular non-covalent bonds formed in crystalline ***α*-BPAN-Br** and ***β*-BPAN-Br**. We believe that the present work demonstrates an efficient method of modulating the properties of piezochromic materials.

Acknowledgements

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Notes and references

[a]*Department of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul, 151-744, Korea. E-mail: jichang@snu.ac.kr;Fax: +82 2 885 1748; Tel: +82 2 880 7190*
[b]*Department of Chemical Engineering, College of Engineering, Soongsil University, Seoul 156-743, Korea.*

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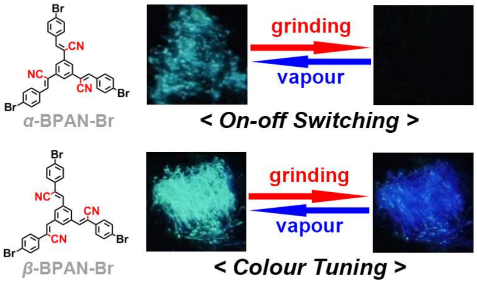
Constitutional isomers of a C_3-symmetric molecule showing different piezochromic behaviours: on-off switching and colour tuning

Yoonbin Lim, Insil Choi, Hyunpyo Lee, Il Won Kim and Ji Young Chang*



Two constitutional isomers of a C_3-symmetric molecule having cyano-vinylene bridges and a phenyl ring core show different piezochromic behaviors, substantial quenching of a bluish green emission (on-off switching) and an emission color change from bluish green to deep blue (color tuning) upon grinding.