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Mechanochromic aromatic hydrocarbons that bear one simple substituent†

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Structurally simple aromatic hydrocarbons that possess only one isocyano group show luminescent mechanochromism. The structural isomers of these aromatic hydrocarbons exhibit blue- and red-shifted emission bands upon mechanical stress. Their low molecular weight enables their sublimation under mild conditions.

Luminescent mechanochromism is a phenomenon that involves an emission-color change in solids or liquid crystals induced by mechanical stimulation such as grinding and pressing.^{1–4} Various organic and organometallic compounds have been reported to show luminescent mechanochromism.^{5–13} So far, a variety of strategies have been developed to generate mechanochromic compounds, including the use of multiple intermolecular interactions,^{7,14,15} connection of donor and acceptor units,^{16,17} controlling dipole moments,¹⁸ and switching between monomeric and assembled states.¹⁹ However, these strategies require mechanochromic compounds with rather complicated molecular structures; thus, low-molecular-weight mechanochromic compounds are still scarce.

Polycyclic aromatic hydrocarbons (PAHs) such as anthracene,^{20–22} pyrene,^{7,23–26} and perylene^{27–29} are among the structurally simplest mechanochromic compounds. These PAHs contain a variety of functional substituents, such as amide, cyano, boronic ester, and alkyl groups and/or linkages to other aromatic or heteroaromatic groups. However, except for an unusual example,³⁰ reports that describe unsubstituted PAHs show luminescent mechanochromism remain elusive. This indicates that the introduction of several substituents or connection to the same or other π -conjugated groups is required to endow simple PAHs with mechanochromic properties. Especially mechanochromic PAHs that bear only one simple substituent remain a rarity.³¹

Here, we report structurally simple monosubstituted pyrene isomers **1** and **4**, which exhibit luminescent mechanochromism. Compared with other reported mechanochromic compounds, the chemical structures of **1** and **4** are relatively simple, *i.e.*, they contain only one isocyano group as a substituent and their molecular weight is low (MW = 227). Solid

samples of **1** and **4** exhibit luminescent mechanochromism with blue- and red-shifted emission bands, respectively. X-ray diffraction (XRD) analyses indicated that the ground phase of **1** is a crystalline phase, while that of **4** is an amorphous phase. The crystal structures revealed the presence of moderate dipole-dipole interactions in the ground phases compared to those in their pristine phases, which is the key for the mechanochromism of **1** and **4**.

Pyrene **4** was prepared from 4-nitropyrene according to a previously reported procedure for monoisocyano PAHs (for details, see the ESI†).³² Pyrene **1**, which has already been reported, was prepared in a similar manner.³³ Although **1** was reported not to show luminescent mechanochromism,³³ we found that both **1** and **4** exhibit luminescent mechanochromic properties.

Under excitation at 365 nm, solid samples of pristine **1** and **4** emit green and blue photoluminescence, respectively (Fig. 1). Crystalline **1** shows an intense green emission with an absolute emission quantum yield (Φ_{em}) of 48% (Table S1†) and an unstructured emission spectrum with a peak at 495 nm (Fig. 2a). Compared with the structured emission of monomeric **1** in CH_2Cl_2 ($c = 5 \mu\text{M}$, Fig. S1b and S2†), the emission maximum wavelength ($\lambda_{\text{em,max}}$) of **1** in the solid state is red-shifted. The average emission lifetime (τ_{av}) of pristine solid **1** is 61 ns, which is longer than that of monomeric **1** in CH_2Cl_2 (13 ns; Fig. S3a and Table S1†). This indicates that the emission of **1** should be characterized as excimer fluorescence.^{23,24,34} Meanwhile, pyrene **4** shows blue emission upon photoexcitation (Fig. 1) with an Φ_{em} of 51% (Table S1†) and a broad emission spectrum with a $\lambda_{\text{em,max}}$ of 452 nm (Fig. 2b), which is shorter than that of **1**. An emission-decay analysis indicated that the τ_{av} of **4** is 38 ns (Fig. S3b and Table S1†), revealing its excimer character.^{23,24,34} The longer $\lambda_{\text{em,max}}$ and τ_{av} of the excimer emission of **1** compared with those of **4** could stem from the stronger interactions of **1** in the excited state.³⁵

To investigate the difference between the $\lambda_{\text{em,max}}$ of pristine **1** and **4**, single-crystal XRD analyses were performed. A single crystal of **1** was obtained from the vapor-diffusion method using CHCl_3 and *n*-pentane. Compound **1** crystallizes in the triclinic *P*1

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† Electronic supplementary information (ESI) available: X-ray crystallographic data, optical-microscopy images, thermal data, emission spectra, and other additional information. CCDC 2312583. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3ra08519h>



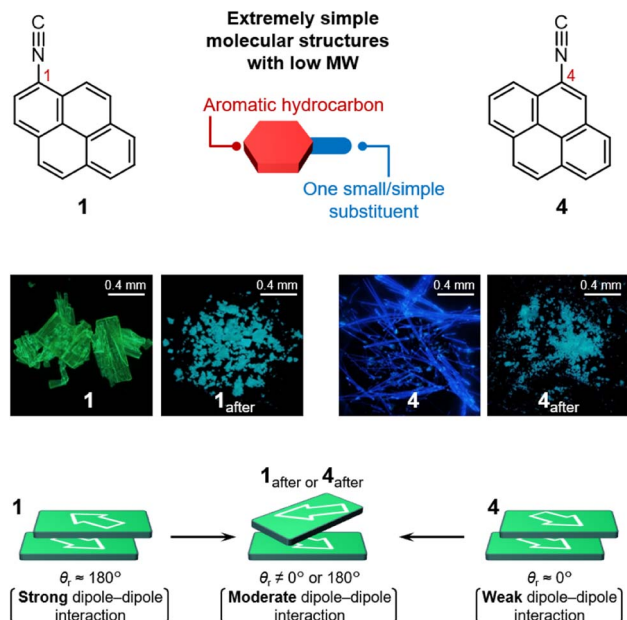


Fig. 1 Chemical structures of **1** and **4**. Photographs of **1**, **1**_{after}, **4**, and **4**_{after} taken under UV light ($\lambda_{\text{ex}} = 365$ nm). Schematic representation of stacked dimers of **1**, **1**_{after}, **4**, and **4**_{after}. Rotation angles of the dipoles of the molecules within the dimer are depicted as θ_r .

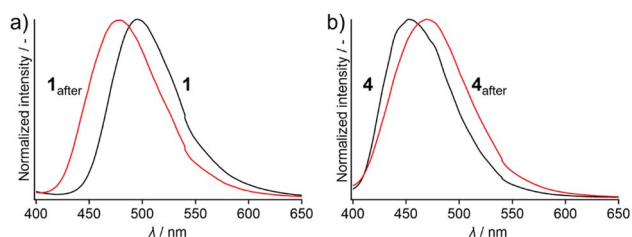


Fig. 2 Emission spectra of solid samples of (a) **1** and **1**_{after} and (b) **4** and **4**_{after} upon excitation at 365 nm.

space group (Fig. 3a and S5 as well as Table S2†).³³ As typically observed for the crystal structures of flat π -systems,^{36,37} **1** adopts a co-facial stacking arrangement in a head-to-tail manner with a rotational angle of the isocyanide groups (θ_r) of $\sim 180^\circ$ (Fig. 3a). These molecules form a one-dimensional (1D) column with an offset along the long axis of the pyrene core (20.97° ; Fig. 3a and S5†) and a short distance of ~ 3.44 Å between the pyrene cores. Single crystals of **4** were also obtained using the vapor-diffusion method with CHCl_3 and *n*-pentane. Compound **4** crystallizes in the monoclinic $P2_1/c$ space group (Fig. 3b and S6 as well as Table S2†) and also adopts a stacking arrangement to form a column with a longitudinal offset along the molecular long axis (25.08° ; Fig. 3b and S6†) similar to that of **1**. However, head-to-head arrangements ($\theta_r \approx 0^\circ$) within the column were confirmed for **4** despite the presence of the electron-withdrawing isocyanide group (the dipole moment of **4** was estimated to be 4.41 D *via* DFT calculations; Fig. S7†). However, the stacking distance between molecules of **4** is relatively short (~ 3.43 Å), which is almost identical to that of **1** with $\theta_r \approx 180^\circ$. Thus, the dipole

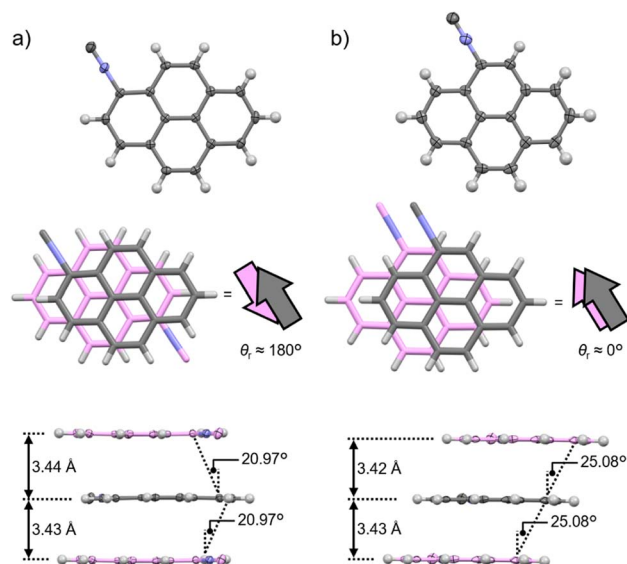


Fig. 3 Molecular structures of (a) **1** and (b) **4** in the single crystal.

moment of **4** should be cancelled out along the *bc* plane, *i.e.*, orthogonal to the stacking direction (Fig. S8†).

The different stacking arrangements of **1** (head-to-tail) and **4** (head-to-head) are most likely responsible for their different $\lambda_{\text{em,max}}$. Considering that the π -stacking distance and offset angles within the co-facial 1D columns of **1** (3.44 Å and 20.97° , respectively) and **4** (3.43 Å and 25.08° , respectively) are close, a similar degree of excimer formation would be expected. However, the $\lambda_{\text{em,max}}$ of **1** (495 nm) is longer than that of **4** (452 nm), which can be attributed to the stronger dipole-dipole interactions of the former as revealed by its head-to-tail arrangement ($\theta_r \approx 180^\circ$). Indeed, structurally simple anthracene molecules have been reported to show longer wavelength emission when excimer formation is assisted by dipole-dipole interactions within the stacked dimers.³⁷ The stronger excimer-like character for the emission of **1** compared to that of **4** is supported by the longer emission lifetime of the former compared to that of the latter (Fig. S3 and Table S1†).

Upon grinding, the emission band of **1** was blue-shifted whereas that of **4** was red-shifted. Upon applying mechanical stimulation using a spatula, the emission color of **1** changed from green to light blue (Fig. 1). The resulting powder, **1**_{after}, showed a broad emission band with a $\lambda_{\text{em,max}}$ of 478 nm (Fig. 2a). Such a blue-shifted emission induced by grinding is less common for luminescent mechanochromic compounds^{38,39} than a corresponding red-shifted emission. The ground powder of **1**_{after} showed an Φ_{em} of 37% and an τ_{av} of 45 ns, indicating excimer-emission character (Fig. S9a and Table S3†).^{23,24,34} In contrast, when pristine **4** was mechanically ground, a red-shifted emission band was observed (Fig. 2b). The ground powder of **4** (**4**_{after}) showed light-blue emission (Fig. 1) with an Φ_{em} of 33% and an τ_{av} of 31 ns (Fig. S9b and Table S3†). This long emission lifetime was attributed to excimer emission.^{23,24,34} The emission spectrum of **4**_{after} is broad and has a maximum at 470 nm, similar to that of **1**_{after} ($\lambda_{\text{em,max}} = 478$ nm; Fig. 2).

Importantly, we confirmed that unsubstituted pyrene molecules exhibit no mechanochromic properties (Fig. S10†), indicating that the introduction of the single isocyanato group endows **1** and **4** with mechanochromic properties.

Powder XRD (PXRD) analyses indicated that **1**_{after} forms a crystalline phase, while **4**_{after} forms an amorphous phase. The PXRD patterns of **1**_{after} and **4**_{after} were compared with those simulated for the corresponding pristine phases derived from the single-crystal coordinates. The simulated pattern of **1** shows three intense diffraction peaks at 9.40°, 10.93°, and 12.10° (black line in Fig. 4a). After applying stress for a short time, new crystalline peaks appeared at 9.47°, 11.31°, and 12.35°, while the original diffraction peaks of **1** remained as shoulders (yellow line in Fig. 4a). This result implies the coexistence of two different crystalline structures of **1** in an intermediate state.⁴⁰ After thorough grinding, the residual shoulders derived from the pristine molecular arrangement disappeared (red line in Fig. 4a), suggesting that the mechanochromism of **1** is based on a crystal-to-crystal phase transition, which is an uncommon phase transition for mechanochromic compounds.^{9,13,25,41,42} Conversely, upon mechanical stimulation of **4**, the intensity of the diffraction peaks (*i.e.*, $2\theta = 10^\circ$ – 12°) of pristine **4** (black line in Fig. 4b) decreased significantly in ground **4**_{after} and no new diffraction peaks emerged (red line in Fig. 4b). This result

indicates that a crystal-to-amorphous phase transition is the origin of the mechanochromism of **4**, which is typically observed for this class of materials.^{8–12,15–17,21,28,39,43,44}

In ground-phase **1**_{after} and **4**_{after}, “moderate” dipole–dipole interactions might be formed compared to pristine **1** and **4**. As mentioned above, the dipole–dipole interactions along the stacking direction in the crystalline phases of **1** and **4** are strong and weak, respectively, as reflected in their corresponding θ_r values ($\sim 180^\circ$ for **1** and $\sim 0^\circ$ for **4**). These extreme θ_r values of the unground phases should become moderate ($\theta_r \neq 0^\circ$ or 180°) upon phase transition into the ground phases irrespective of the crystalline (**1**_{after}) or amorphous phases (**4**_{after}, Fig. 5). This result indicates that the dipole–dipole interactions are most likely weakened after the phase transition from **1** and strengthened from **4** in terms of θ_r upon grinding (Fig. 5). This is consistent with the blue-shifted emission of **1** and the red-shifted emission of **4**. Generally, in addition to θ_r , dipole–dipole interactions are also affected by the torsional angles and distance between the π planes relative to the stacking direction (Fig. S11†).⁴⁵ However, the lack of a detailed crystal-structure analysis for unknown crystalline **1**_{after} and amorphous **4**_{after} at this stage hindered unveiling the effect of the torsional angles and distances on the emission wavelength.

Upon thermal treatment, pristine **1** and **4** exhibited a similar behavior to that induced by mechanical stimulation. Thus, heating a pristine solid sample of **1** to 100 °C resulted in an emission-color change from green to light blue (Fig. S12a†). The resulting light-blue emission of **1** remained intact upon cooling to room temperature (Fig. S12a†). The light-blue-emitting crystals of **1** can be regarded as **1**_{after} because their emission spectrum and PXRD patterns are similar to those of **1**_{after} obtained from mechanical stimulation (Fig. S12b and S12c†). Differential-scanning-calorimetry (DSC) studies of **1** confirmed a thermal phase-transition temperature of 100 °C (Fig. S13 and S14†).⁴⁶ Similar to **1**, a solid sample of **4** showed thermoresponsive behavior similar to that observed upon mechanical stimulation, *i.e.*, thermo-induced amorphization of **4** led to a red-shifted emission band (Fig. S15†). These results indicate that mechanical stimulation and thermal treatment induce the same phase transitions in **1** and **4**, leading to clear luminescent chromic behavior.

Compounds **1** and **4** are the luminescent mechanochromic compounds with one of the lowest molecular weights (MW = 227) reported to date.⁴⁷ Accordingly, we expected that it should be possible to sublime **1** and **4** under mild conditions,

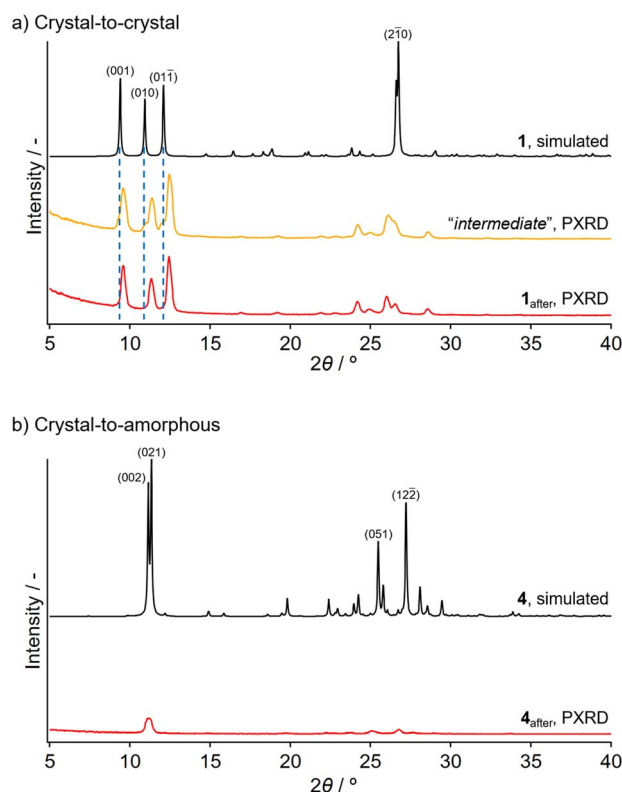


Fig. 4 Simulated PXRD patterns of pristine forms derived from the single-crystal structures (black lines) and experimental PXRD patterns of the ground powders (red lines) of (a) **1** and (b) **4**. The yellow line in (a) is the PXRD pattern of the “intermediate” sample of **1**, which was obtained from grinding for a short time. Miller indices are shown for four intense diffraction peaks of the simulated powder patterns of **1** and **4**.

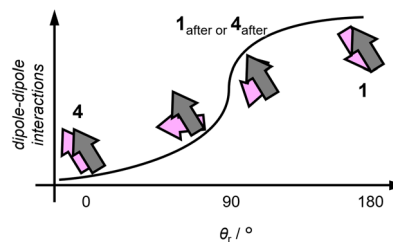


Fig. 5 Schematic representation of the relationship of θ_r within the co-facial arrangements of the dipoles (depicted by arrows) in the stacked dimer and the strength of the dipole–dipole interactions.



potentially enabling the low-cost preparation of thin films. To confirm this hypothesis, we conducted preliminary sublimation experiments. After placing a solid sample of **1** in a round bottom flask and reducing the pressure to 2.5 mbar while slowly increasing the temperature, sublimation started at 40 °C (Fig. S16a†). ¹H NMR and polarized-optical-microscopy analyses confirmed that the sublimated solid is **1**, *i.e.*, **1** did not undergo decomposition and maintained crystallinity (Fig. S16b and S17†).⁴⁸ A similar result was observed for pyrene **4**, *i.e.*, sublimation occurred at 2.5 mbar and 50 °C (Fig. S18 and S19†). Such mild sublimation conditions (moderate pressure/low temperature) might enable the cost-efficient preparation of large thin films. A more detailed analysis of the sublimation properties, *i.e.*, determination of the vapor pressure, and preparation of thin films with a single domain of **1** and **4** will be the subject of future work.

Conclusions

We have reported that structurally simple pyrene molecules **1** and **4**, which bearing only one small isocyano group, exhibit luminescent mechanochromism. Upon exposure to mechanical stress, **1** showed a blue-shifted emission band as a result of a crystal-to-crystal phase transition, while **4** exhibited a red-shifted emission as a result of amorphization. The crystal-structure analyses of **1** and **4** indicated that the change in the strength of the dipole–dipole interactions with neighboring molecules is the origin of their opposite emission-color changes. The low molecular weight of these compounds enables their sublimation under mild conditions (2.5 mbar and 40–50 °C). This study thus offers a new molecular-design strategy to obtain mechanochromic compounds based on the connection of one aromatic core and one small substituent.

Author contributions

TS designed the project; KH performed and analyzed the experiments with guidance from TS; TS wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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- 47 For structurally simple luminescent pyrene molecules without mechanochromic properties, see: ref. 36. For mechanochromic compounds with low molecular weight (MW = 218–271), see: refs. 16, 43, and 44.
- 48 Under these conditions, the single crystallinity of the sublimated samples of **1** could not be confirmed.

