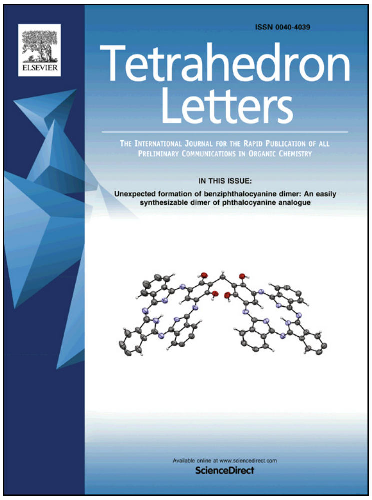

D-A-D type dinitriles with vapor-dependent luminescence in the solid state

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PII: S0040-4039(17)31204-2
DOI: https://doi.org/10.1016/j.tetlet.2017.09.068
Reference: TETL 49338

To appear in: *Tetrahedron Letters*

Received Date: 20 August 2017
Accepted Date: 22 September 2017

Please cite this article as: Furuyama, T., Shinozaki, J., Tasso, T.T., Maeda, H., Segi, M., Kobayashi, N., D-A-D type dinitriles with vapor-dependent luminescence in the solid state, *Tetrahedron Letters* (2017), doi: https://doi.org/10.1016/j.tetlet.2017.09.068

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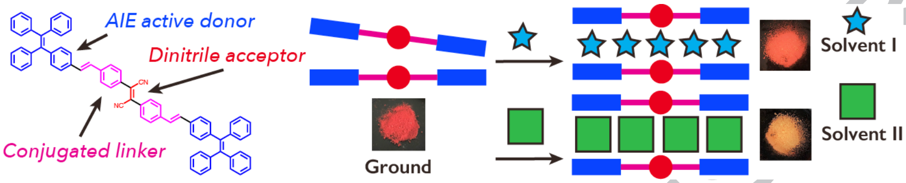

Tetrahedron Letters
journal homepage: www.elsevier.com

D-A-D type dinitriles with vapor-dependent luminescence in the solid state

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Cyanides
Aggregation
Fluorescence
Mechanochromism
Vapochromism

ABSTRACT

D-A-D (Donor-Acceptor-Donor) type dinitriles linked by a styryl (**1**) or phenylethynyl (**2**) group have been prepared. A styryl or phenylethynyl group introduced to increase the flexibility and the size of the π-conjugation. Both compounds showed strong emission in the solid state, AIE (aggregation-induced emission) behavior, and mechanochromism. The fluorescence color of ground powder changed by organic solvent vapor (vapochromism). Especially, the color of styryl-linked **1** after exposures depends on the solvent, while the color of **2** is the same after exposure to different solvents. Single crystal and powder XRD measurements revealed multi-state microcrystalline structures of **1** by the flexible styryl linker that leads to a loose crystal packing. This methodology based on the flexible linker allows for the detection of small organic molecules without transition metals.

Organic materials whose spectral arrangement of optical properties is changed by weak external stimuli (chromic responses) are one of the most attractive targets in chemistry, as well as in material and biological sciences. In this regard, π-conjugated organic compounds are good candidates, since their properties can be fine-tuned by synthetic modifications. Various materials with chromic responses, such as photochromism, solvatochromism, halochromism, thermochromism, mechanochromism, and vapochromism have been synthesized. Although some responses occur in solution, mechanochromism and vapochromism appear only in the solid state. Chromic responses in emission properties in the solid or aggregated state are required for applications in solar cells, probes for bioimaging, photosensitizing agents and sensors of toxic volatile organic compounds (VOCs).[1] However, the emission of typical π-conjugated compounds is almost entirely quenched in the solid state due to an aggregation-caused quenching (ACQ) effect,[2] so that reversibly controlling the emission properties by mechanical forces and/or vapors is an attractive challenge in modern material chemistry.

In this communication, we report the synthesis and multi-chromic properties of D-A-D (Donor-Acceptor-Donor) type dinitriles. Classical optical probes show only one response to various kinds of external stimuli, however, for the detection of small molecules such as VOCs in the air and biological signals in cancer and other diseased tissues, more than two emissive states should be coupled with specific molecular inputs.[3-4] Vapochromism, for instance, is still rare for organic conjugated compounds without transition metals,[5-6] with the exception of a response with acid/base vapor fuming (a kind of halochromism).[7] Tetraphenylethylene (TPE) is known to be a key moiety not only for aggregation-induced emission (AIE) behavior, but also for various chromic responses in organic materials.[8-9] Recently, we found that the TPE-linked dinitrile (**TPE–CN$_2$**, Scheme 1) showed strong emission in the solid state, AIE behavior and chromic responses to mechanical forces.[10] Although **TPE–CN$_2$** showed vapochromism as well, the colors after fuming did not depend on the solvent used. Various dinitrile derivatives have been synthesized as precursors of tetraazaporphyrins and dinitrile derivatives with appropriate donor moieties show intense emission in the solid state.[11] The vapochromic response of transition metal-containing organometallic materials originates from changes in metal-metal interactions.[12] In this sense, another strategy is required to develop pure-organic vapochromic materials which can respond to various kinds of vapor. While host-guest chemistry is often efficient for overcoming this problem,[13-14] we focused on the flexibility of molecules. By introducing flexible moieties into molecules with chromism in the solid state, we anticipated that the microcrystalline structure of the flexible π-conjugated chain might change on extra weak external stimuli, such as simple, neutral solvent vapors. To increase the flexibility and the size of the π-conjugation, styryl

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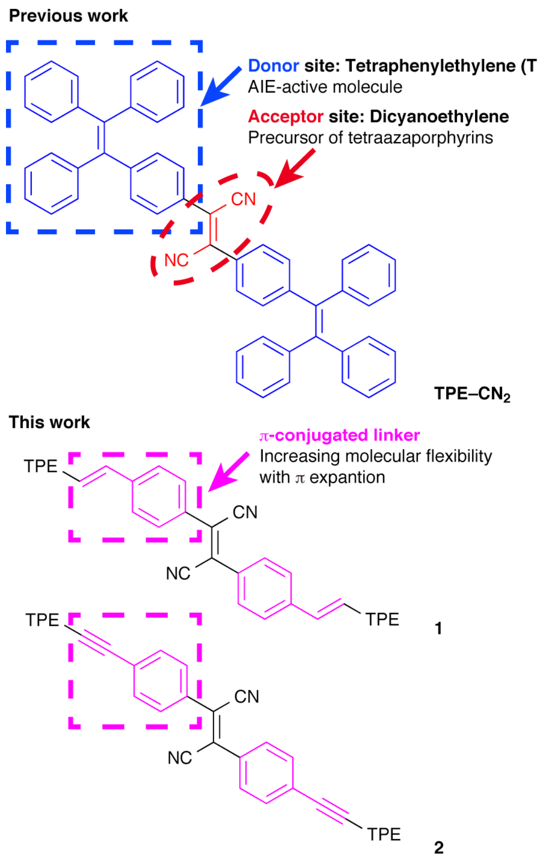
(**1**) or phenylethynyl (**2**) groups[15-16] were introduced between the TPE and dinitrile moieties of **TPE-CN$_2$**.



Scheme 1. Molecular Structure of dinitirles **1** and **2** in this work.

The synthetic procedure of **1** and **2** is shown in Scheme S1 (see Supporting Information). Dinitrile derivatives could be synthesized by dimerization of phenylacetonitrile derivatives.[17] Vinylene-bridged TPE-phenylacetonitrile **4** was obtained from TPE-Br **5** and 4-cyanomethylstyrene by the Heck reaction. After dimerization, **1** was obtained as a mixture of *E* and *Z* forms at a dinitrile moiety. However, the *Z*-form **1** was isomerized to a mixture of *E* and *Z* rapidly in solution under ambient light (data is not shown). The pure *E*-form **1** suffered no isomerization after irradiation with UV-light (365 nm) for 1 min in solution (Fig. S1, see Supporting Information), so it was used for characterization of the structure and investigation of the optical properties, assuming negligible isomerization during these experiments. When equilibrium was reached (ca. 1 hour), the *E/Z* ratio found was 73/27. Hence the *E* form of **1** is more favorable. No isomerization was observed on irradiation of the samples with light in the solid state. **2** was synthesized from bis(4-bromophenyl)fumaronitrile (**8**, *E* form) and TPE-ethynylene **7** by the Sonogashira reaction. Only the *E*-form **2** was obtained, since bis(4-bromophenyl)maleonitrile (*Z* form) could not be produced by the dimerization of (4-bromophenyl)acetonitrile.[17] **1** and **2** could be fully characterized by ^{1}H and ^{13}C NMR and HR-FAB mass spectrometry.

The structure of **1** was unambiguously elucidated by X-ray diffraction analysis of crystals obtained from the diffusion of methanol into a THF solution (Fig. 1). Unfortunately, suitable single crystals of **2** could not be obtained. All three vinylene moieties were *E* form (Fig. 1a). A crystal packing diagram of the crystals is shown in Fig. 1b, in which THF molecules were found in the unit cell (the crystal is denoted as **1**⊃THF). **1**⊃THF showed a 1D-layer structure in the crystal, with THFs oriented between the layers, where the distances of the intermolecular layers are 3.658 and 4.874 Å (Fig. S2, see Supporting Infromation). The TPE moieties were oriented in a twisted manner, indicating weak intermolecular π-π stacking interactions. The flexible styryl linker of **1** may lead to a loose crystal packing, resulting in solvent molecules delocalized on the entire molecule. The single crystal structure of **TPE-CN$_2$** from a chloroform/methanol mixture,[10] on the other hand, contained chloroform molecules localized only on the dicyanoethylene moiety (Fig. S3, see Supporting Infromation) indicating a more rigid packing structure.

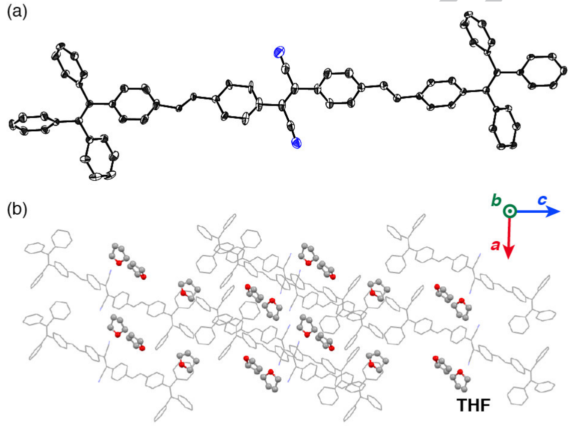


Fig. 1. a) X-ray crystal structure of **1**. The thermal ellipsoids were scaled to the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. b) Packing diagram of **1**⊃THF. Hydrogen atoms are omitted for clarity.

Absorption and emission spectra of diluted solutions of these compounds are shown in Fig. S4 (see Supporting Information), with a summary of the absorption and emission properties in solution listed in Table S3 (see Supporting Information). Both compounds absorb light around 400 nm, and solvent effects in the absorption properties are low. Calculated absorption spectra (Fig. S5, see Supporting Infromation) reproduced their absorption properties. The intense absorption band could be assigned to an intramolecular charge-transfer (CT) transition from TPE to dinitrile moieties. This is consistent with their emission spectra in various solvents, which significantly redshifted on increasing the solvent polarity. To quantify the solvatofluorochromism of these compounds, Lippert-Mataga plots[18] were made (Fig. S4c, see Supporting Infromation). On linear fitting, large slopes were found for **1** (6.1 x 10^3) and **2** (5.1 x 10^3), which represent similar solvatofluorochromism to previously reported D-A type chromophores (**TPE-CN$_2$**: 7.9 x 10^3).[10] **1** and **2** showed typical AIE behavior in THF/water mixed solvents (Fig. S6, see Supporting Infromation). The fluorescence intensity was sharply increased with increasing water content, indicating that the molecules aggregate with increasing amounts of poor solvent. The 5- and 58-fold increase in the intensity at the fluorescence peak of compounds **1** and **2** observed in the mixture containing 90% water substantiated a strong AIEE effect.

Fig. 2 shows emission spectra of the compounds in the solid state. In the as-prepared, dried powder, the emission peak of **1** (617 nm) appeared at a longer wavelength than that of **2** (574 nm). An additional intermolecular packing interaction may exist for **1**, because the obtained structure of **1** in **1**⊃THF is slightly different from the calculated structure (as gas phase) of **1** (Fig. S7, see Supporting Infromation). After the powders of **1** and **2** were exposed to toluene vapor, the emission peaks were blue-shifted, and visible color changes were observed. The emission peaks were returned to the initial state after grinding the powder.

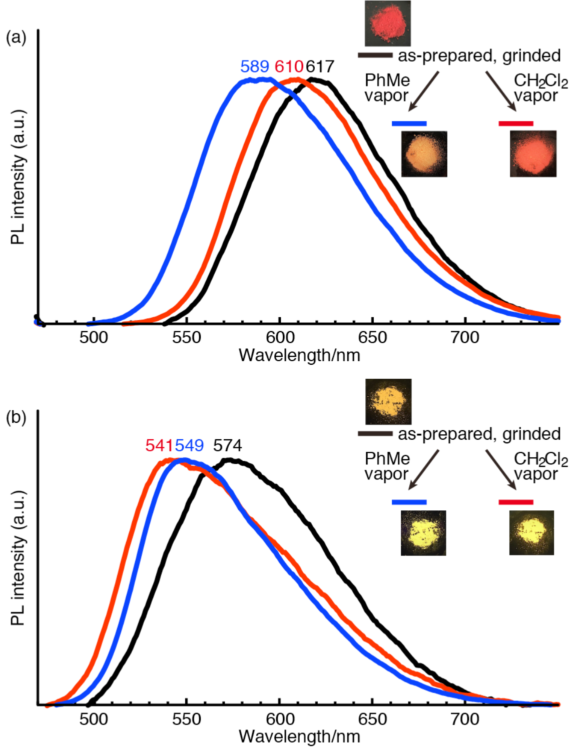


Fig. 2. Changes in the fluorescence spectra of a) **1** and b) **2** on external stimuli. Excitation at 442 and 411 nm for **1** and **2**, respectively. Photos were taken under UV light irradiation (365 nm).

Therefore, compounds **1** and **2** showed mechano-/vapochromic responses. For a demonstration of mechanochromic applicability, the powder of **1** was dispersed on filter paper, and some characters were written by scratching (Fig. S8, see Supporting Infromation). On fuming the paper with toluene, the characters became invisible, and this writing/erasing process could be repeated reversibly. Powder XRD (PXRD) measurements revealed a microcrystalline phase-transition of **1** and **2** during the grinding/fuming cycle (Fig. S9, see Supporting Infromation). On grinding, the reflection peaks became weaker and broader, indicating an emergence of amorphous character as a result of the application of an external mechanical force to the powder. After fuming with toluene, the peaks were regenerated. The positions and intensities of the peaks completely matched between the first and second fuming cycles, thus indicating that the microcrystalline structure was regenerated reversibly by fuming with organic solvents. These chromic responses of **1** and **2** were also induced by dichloromethane vapor. Interestingly, the color of ground **1** was changed from red to reddish-yellow by dichloromethane vapor, while the color was changed from red to orange by toluene vapor (Fig. 2a, inset). On the other hand, the color difference of **2** after exposure to toluene or dichloromethane vapor was negligible. The fluorescence spectra of **1** after exposure to various solvents revealed that the color after fuming depended on the type of solvent (Fig. S10, see Supporting Infromation). Among five solvents which gave a vapochromic response, the emission peak shifted from dichloromethane (610 nm) to toluene (589 nm), which was enough to produce a visible color change in the powder. The solubility of **1** appeared important for the color change, so that the exposure of hexane vapor to ground **1** did not change the color (note that **1** does not dissolve in hexane). With respect to the solvatofluorochromism of **1** in solutions, after exposure to vapor, the fluorescent peak shifted to the blue on decreasing the solvent polarity.

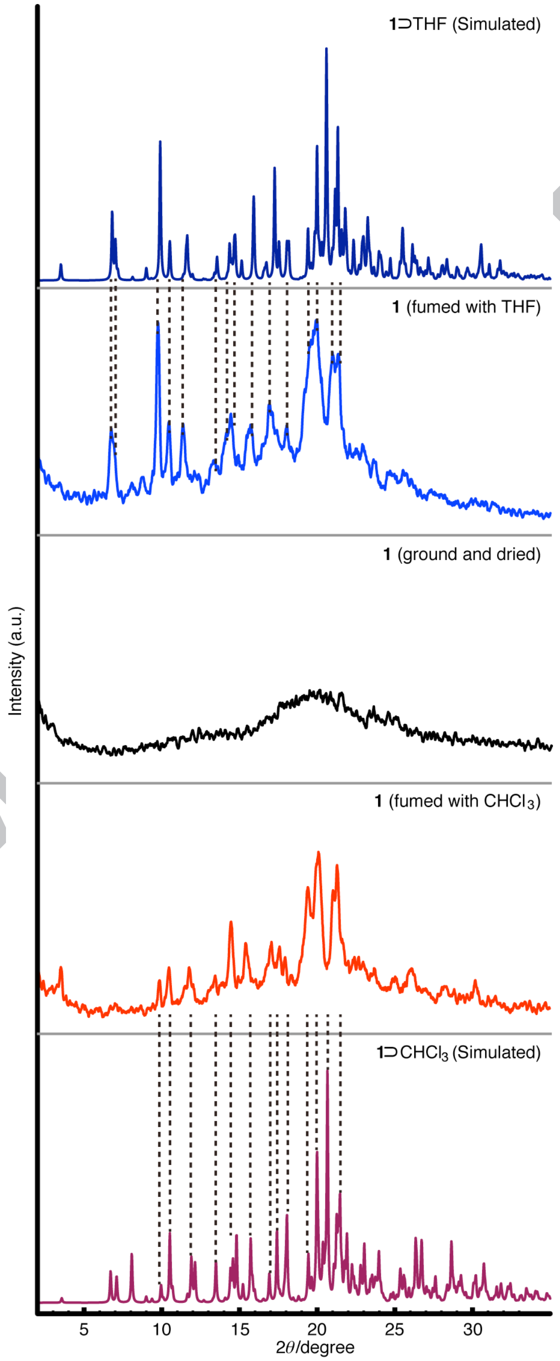


Fig. 3. Experimental XRD patterns of dried **1**, **1** with THF vapor and **1** with $CHCl_3$ vapor and simulated pattern for the single crystal structure of **1**⊃THF and **1**⊃$CHCl_3$.

The difference in vapochromic responses was clarified by PXRD measurements. In the case of **2**, the pattern after exposure to dichloromethane vapor became identical to that after exposure to toluene vapor (Fig. S11, see Supporting Infromation). Thus, solvent molecules were essential for the regeneration of the microcrystalline structure of **2**, but the solvent molecules did not affect the final microcrystalline structure due to the rigid ethynylene linkage in **2**. Fig. S12 (see Supporting Infromation) shows PXRD patterns of powder **1** after exposure to solvents that give vapochromic behavior. The differences in the peaks are relatively small; however, each pattern can be distinguished. The contact with organic solvent vapor may form thin liquid layers on the surface of **1**,[19] then the solvent molecules penetrate into the amorphous structure, generating the microcrystalline structure. Simulated PXRD patterns determined from single crystal X-ray structures obtained from THF/methanol (**1**$\supset$THF) or chloroform/methanol (**1**$\supset$CHCl$_3$)[20] solution are shown in Fig. 3 in order to understand the vapor-dependent color change in **1**. The simulated PXRD pattern of **1**$\supset$CHCl$_3$ is different from that of **1**$\supset$THF, which agreed with the experimental PXRD pattern of powder **1** after exposure to fuming chloroform or THF. The packing structure of **1**$\supset$CHCl$_3$ also showed a 1D-layer structure, with chloroform molecules oriented between the layers. On the other hand, the distances of the intermolecular layers were changed (4.862 Å and 3.621 Å) in relation to the size of the solvent molecules (Fig. S13, see Supporting Infromation). Previously reported single crystal structures of TPE-based vapochromic molecules (solvent dependency was not found or discussed) showed no solvent molecule on specific sites.[10,21-22] Hence, the styryl linker is considered to be important for obtaining the solvent dependent multi-microcrystalline structures in this study. Since the position of the fluorescence peak depends on the stacked structure of π-conjugated molecules,[23] the color changes after fuming can be assigned to the difference in spacing between the layers in microcrystalline arrays.

In summary, dinitrile derivatives exhibiting multi-luminescence responses with mechanical grinding and exposure to vapors of organic solvents have been synthesized. The D-A-D system and TPE moieties show efficient emission in the visible region and AIE properties. Phenylethynyl-linked **2** exhibits an obvious AIEE effect, and a 58-fold increase in fluorescence intensity after aggregation. Mechanical grinding of powder samples changes the emission color of the samples, and exposure to an appropriate organic vapor for several minutes was sufficient to reversibly regenerate the original color. A flexible π-conjugated linkage is important to distinguish the kind of organic solvent. The color of styryl-linked **1** after exposures depends on the solvent, while the color of **2** is the same after exposure to different solvents that show a chromic response. The differences between **1** and **2** could be clearly explained by the PXRD spectra of grinding and fuming samples. PXRD patterns of **1** after exposure to solvents showed multi-microcrystalline arrays that depend on the solvent. The single crystal structure of **1** supported the PXRD patterns, and the spacings of the intermolecular layers were changed by solvent molecules. Compound **1** is easy to synthesize and free from expensive and/or toxic transition metals, being a so-called "smart" material which is able to distinguish the type of organic solvent by visible color changes. This kind of material will be applied to novel sensors for the detection of small organic molecules in the fields of environmental and agricultural sciences. Further work is currently underway to expand the scope of substrates to change the colors by the introduction of additional functional moieties and to shift emission colors to the near-IR region for biological applications.

Acknowledgments

This work was partly supported by a JSPS KAKENHI Grant (No. 15K05409), The Foundation for Japanese Chemical Research, Hokuriku Bank Foundation, The Murata Science Foundation and Kanazawa University SAKIGAKE Project. The authors thank Prof. Shigehisa Akine, Prof. Tetsuya Taima, Prof. Tomoki Ogoshi, Prof. Makoto Karakawa, Dr. Yoko Sakata and Dr. Takahiro Kakuta (Kanazawa University) for physicochemical measurements.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.XXXX.XX.XXX.

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Highlights:

D-A-D type dinitriles linked by flexible linkers have been synthesized.
The vapochromic response of the styryl-linked compound is solvent dependent.
These materials can distinguish different organic solvents without metals.