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Charge-Transfer Interactions

A Photoswitchable and Photoluminescent Organic Semiconductor Based On Cation–π and Carboxylate–Pyridinium Interactions: A Supramolecular Approach**

Sandipan Roy, Suvra Prakash Mondal, Samit K. Ray, and Kumar Biradha*

The design and discovery of novel organic electronic materials still poses a major challenge owing to their utility in field-effect transistors,[1] memory devices,[2] solar cells,[3] light-emitting diodes,[4] displays, and plastic electronics.[5] The organic materials are of interest for designing electronics because of their easy fabrication, modulation capabilities, and cost-effectiveness. Several polyaromatic materials, such as tetracene, pentacene, perylene, and rubrene, were shown to be semiconductors owing to the existence of aromatic–aromatic interactions.[6] Studies on tetrathaiafulvalene (TTF), which is a prototypical organic semiconductor, reveal the increase in charge mobility when TTF molecules are assembled through face-to-face aromatic interactions.[7] Furthermore, TTF and tetracyanoquinodimethane (TCNQ) are known to form strong charge-transfer complexes and exhibit metallic conductance.[8] Similarly, donor–acceptor charge-transfer (CT) complexes of TTF-imidazole with TCNQ, *p*-benzoquinone, and anilic acid-type acceptors exhibit a number of conducting and semiconducting materials.[9] Despite of these potential examples based on charge-transfer interactions, very few attempts have been made to design new molecular organic semiconductors[10] using crystal engineering strategies.[11]

Recently, the organic salt of tetraphenylethylene tetracarboxylic acid with 4,4′-bispyridyl ethylene was shown to exhibit semiconducting characteristics ($\mu_{eff} = 0.38$ cm^{2}V^{-1}s) owing to the presence of charge-assisted hydrogen bonding.[10c] On the other hand, photochromic materials, which can change their color and properties upon irradiation by light, are of importance for optical information storage and photonic switches.[12] To date, many organic molecules have been shown to be semiconductors, many have been shown to be photochromic and many have been shown to be photoluminescent. To the best of our knowledge, no organic materials have been shown to contain all these three proper-

ties in combination. One of the early examples of exhibiting semiconductivity and photochromism is triphenylformazan based on *cis–trans* isomerization upon photoirradiation.[13] Alternately, such materials are designed by incorporating photochromic molecules as a side chain to π-conjugated polymers.[14] However, to the best of our knowledge, the multicomponent organic supramolecular photochromic material with switchable electrical conductivity has not been reported to date.

Herein we report a crystal engineering strategy for the synthesis of supramolecular two-component organic material that exhibits reversible photochromism (yellow↔green) and reversible conductivity (low conductivity↔high conductivity). Carboxylic acid- and pyridine-containing molecules are known to form two component materials by COOH and pyridine hydrogen-bonding interactions. These materials can be termed as either cocrystals (O−H···N) or salts (N$^+$−H···O$^-$) based on the position of the proton involved in the interaction. During our ongoing crystal engineering studies on exploring the hydrogen-bonded networks of co-crystals or salts of H$_4$1 with various bis(pyridyl) derivatives, we have
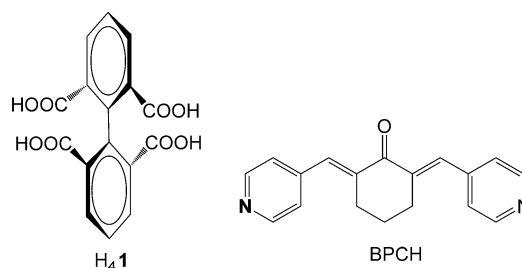
serendipitously discovered a material that not only exhibits semiconductivity but also photochromism and photoluminescence. Recently, we have shown that the complexation reactions of H$_4$1 with bis(pyridyl) derivatives result in the formation of either two-dimensional or diamondoid networks.[15] These materials have shown remarkable capability for the inclusion of various aromatics by cation–π interactions, which ultimately served as colorimetric indicators for the identification of aromatic compounds.[16]

The complexation reaction of 2,2′,6,6′-tetracarboxybiphenyl (H$_4$1) with 2,6-bis(4-pyridyl methylidene) cyclohexanone (BPCH) in MeOH resulted in yellow single crystals of [H$_2$1][H$_2$BPCH]·H$_2$O (2). The asymmetric unit in the crystal structure of 2 consists of one unit each of H$_2$1, H$_2$BPCH, and a water molecule. The H$_2$1 moiety contains two intramolec-

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ular hydrogen bonds between the deprotonated carboxylate oxygen atoms and COOH groups (O–H···O: 2.522 Å, 174.10°, 2.559 Å, 169.72°), and these anions are linked by H$_2$BPCH units by charge-assisted and donor-bifurcated N$^+$-H···O$^-$ hydrogen bonds (N–H···O: 2.828 Å, 147.01°; 2.897 Å, 147.91°, 2.631 Å, 169.26 Å) to form a discrete four-component assembly (Figure 1). Within the assembly, the two inversion-
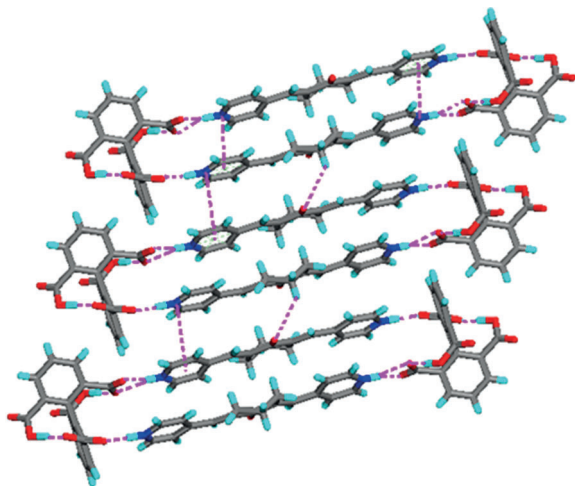

Figure 1. Representation of the crystal structures of **2** or **3**: Formation of tetrameric assemblies by π–π interactions and their packing; notice various type of interactions involved within the assembly. C gray, O red, H pale blue, N dark blue.

related H$_2$BPCH units pack on each other by strong cation–π charge transfer interactions between the two pyridinium rings, and the distance between N$^+$ to the centroid of pyridinium ring is 3.482 Å. Furthermore, one of the carboxylate moieties that is situated on top of the nitrogen atom of pyridinium ion is also engaged in a COO$^-$···N$^+$ interaction exhibiting a N$^+$–O distance of 3.369 Å. Furthermore, the discrete assemblies pack on each other such that there are infinite stacks of cation–π charge transfer interactions.

The crystals of **2** were found to exhibit photochromism; they turn from yellow to deep-green-colored crystals (**3**) upon exposure to sunlight (Figure 2a) within a few minutes. The crystals of **3** are found to be stable and remain green for more than two months in room light or in the dark. Nonetheless, the reverse transformation, that is **3** to **2**, was found to occur by heating the crystals at 80°C in room light. The single-crystal X-ray structure determination of **3** indicates that the color change from yellow to green occurred without any apparent changes in the structural arrangement, making it difficult to understand this phenomenon by X-ray crystallography. However, these two forms were distinguished easily by solid-state diffuse reflectance spectra (DRS): the yellow form exhibits only one absorption maxima at 450 nm, whereas the green form exhibits two absorption maxima at 450 nm and 755 nm (Figure 2b).

The appearance of the new broad band at 755 nm for **3** indicates the augmentation of charge-transfer interactions, which may be by the formation of a free radical that resulted in the change of color to intense green. The generation of
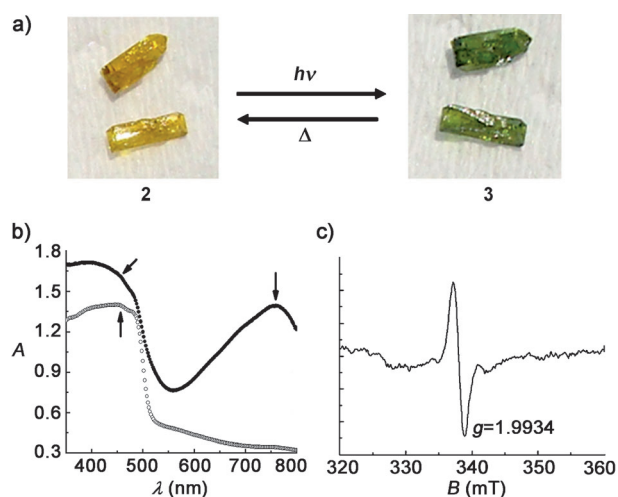

Figure 2. a) Illustration of photochromism reaction with snapshots of the crystals of compounds **2** and **3**. b) UV/Vis diffuse reflectance spectra of **2** (non-irradiated; ○) and **3** (irradiated; ●) Arrows indicate absorption maxima. c) EPR spectrum for the crystals of **3**.

radicals was confirmed by recording electron paramagnetic resonance (EPR) spectra for the samples of **3**. The solid sample of **3** show a sharp radical signal at around $g = 1.99$ in X-band EPR at room temperature (Figure 2c). The presence of radicals was also found in the solid sample of **2**, albeit at a lower concentration than that of **3.** These studies clearly indicate that the photochromism process is accompanied with the generation of radicals.

The existence of free radicals coupled with cation–π interactions and charge-assisted hydrogen-bonding interactions prompted us to study the electrical conductivity of these materials before and after irradiation. Therefore, the current–voltage (I–V) characteristics of specially prepared microcrystalline powders of **2** and **3** were measured using conducting probe atomic force microscopy (CP-AFM), by uniformly dispersing the samples of **2** and **3** on thermally evaporated Au coated SiO$_2$/p-Si substrates and imaged to determine the crystal morphology and shape (Figure 3a). The presence of SiO$_2$ intermediate layer eliminates the role of silicon substrate in the current conduction and ensures the current flow only through the sample. The I–V characteristics are measured with CP-AFM by applying a sample bias voltage of ±1 V.

The nonlinear behavior of the I–V curves clearly demonstrates the semiconducting nature of **2** and **3** (Figure 3b). Furthermore, it is evident from the I–V curves that the material **3** is highly conductive compared to material **2** in the applied bias range. The resistivity (ρ) values for **2** and **3** were calculated using the relation $\rho = RA/L$, where R is the resistance, A is the probe–sample contact area, which is calculated (see the Supporting Information) using the Hertzin elastic model,[17,18] and L is crystal height, which is measured from AFM image. The values of R for the samples **2** and **3** were obtained from the linear region of I–V curves in the bias range of ±0.12. The resistivity (ρ) values of **2** and **3** were found to be 9.98 ± 0.40 Ω cm and 0.64 ± 0.11 Ω cm, respectively. Using the ρ values, the conductivity (σ) values for **2** and **3** were calculated to be 0.10 ± 0.05 S cm^{-1} and $1.55 \pm$
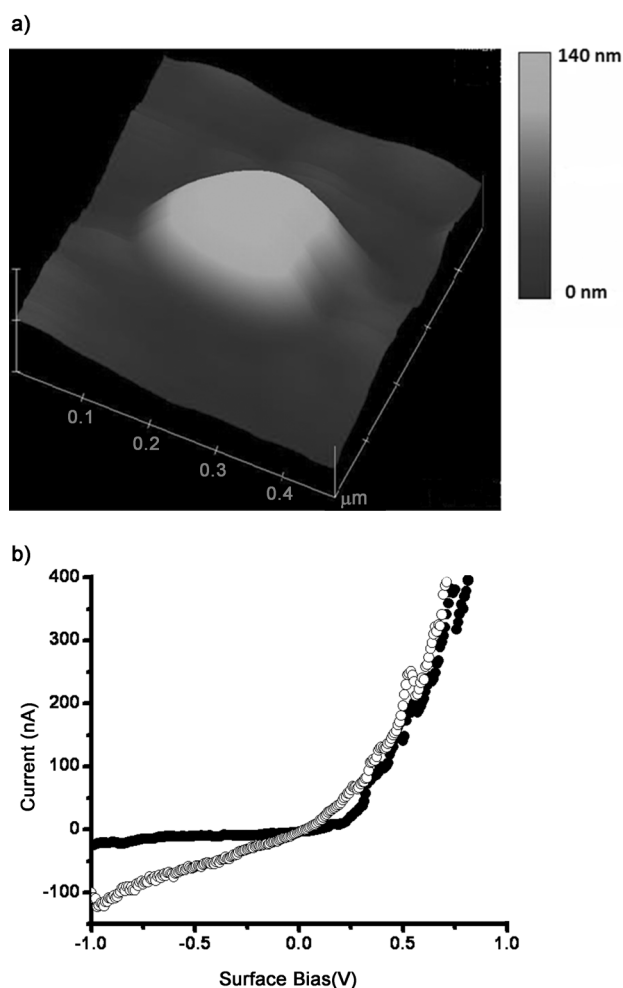
a)

b)

Figure 3. a) Representative 3D crystal image for **2**. b) *I–V* curves for **2** (●) and **3** (○).

The emission spectra, upon excitation at 325 nm, show a clear hump at about 460 nm and a strong green emission peak at 530 nm (Figure 4a). The emission peak at around 460 nm (ca. 2.6 eV) is attributed to the HOMO–LUMO
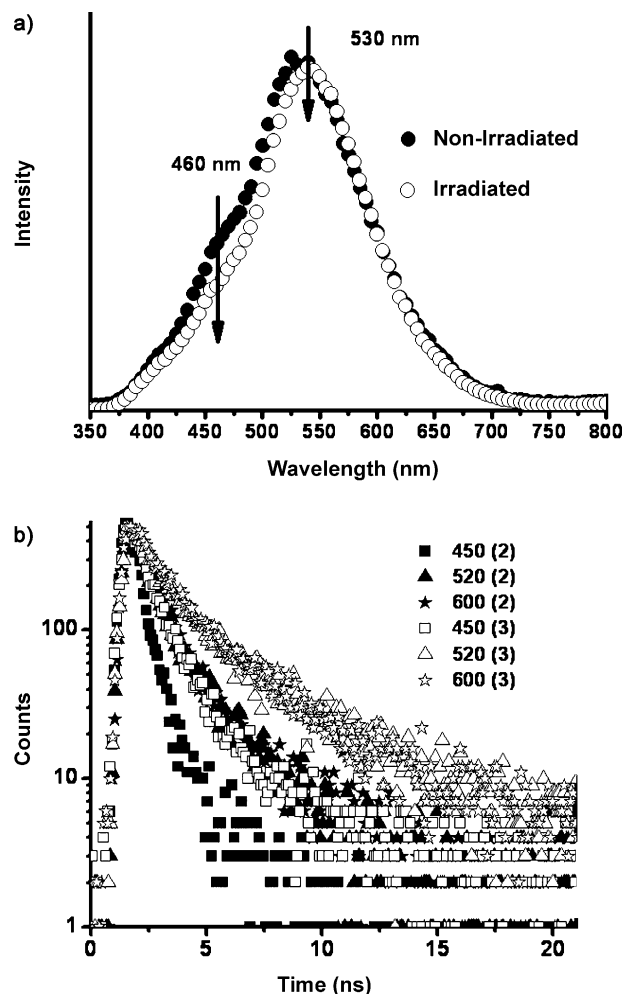
a)

b)

Figure 4. a) Normalized photoluminescence spectra of **2** (●) and **3** (○). b) Fluorescence decay curves for **2** (filled symbols) and **3** (open symbols) at 450 (■,□), 520 (▲,△), and 600 nm (★).

0.20 S cm^{-1}, respectively. From these values it is evident that the **3** is nearly 16 times more conducting than **2**. Furthermore, the effective charge mobilities μ for **2** and **3** are 0.174 ± 0.09 cm^{2}V^{-1}s and 1.40 ± 0.10 cm^{2}V^{-1}s, respectively, which are estimated using equation $\mu = \sigma^{0.76}$ that was developed by Brown et al. for an organic semiconductor.[19] It may be noted that these values are higher than those of well-established conjugated polymers and other single-crystalline organic semiconductors.[14,20,21] This clearly demonstrates the efficacy of supramolecular material exhibiting photochromic behavior with high charge mobility, which is attractive for a highly sensitive organic semiconducting material.

The solid-state luminescence for a semiconducting material is of particular interest for designing organic light-emitting diodes (OLEDs) and displays.[4,22] However, the existence of strong π–π interactions in crystalline semiconducting organic materials most often leads to suppression of the luminescence property. Therefore, it is extremely difficult in designing the organic semiconducting material with considerable emission efficiency. In the present case, it was found that both the materials exhibited similar emission spectra owing to the use of highly intense UV laser (laser power ca. 25 mW), which spontaneously converted the sample **2** into **3**.

transition. Furthermore, the time-resolved photoluminescent measurements for **2** and **3** were carried out to understand the differences in charge transfer through a localized level. Figure 4b shows the decay characteristics of non-irradiated (**2**) and irradiated crystals (**3**) monitored at emission wavelengths 450 nm, 520 nm, and 600 nm. These decay studies clearly demonstrate that the irradiated crystals (**3**) have longer lifetime compared to non-irradiated samples (**2**). It indicates the presence of additional electronic states for the longer relaxation of electron during the transition in **3**.

In summary, we have demonstrated that the supramolecular material (**2** and **3**) exhibits a unique combination of photochromism, semiconductivity with charge mobility up to 1.40 cm^{2}V^{-1}s, and emission properties. These materials can be easily prepared by mixing two structurally simple and easily accessible molecules in MeOH. The photochromism

mechanism was clearly shown to occur through free radical formation, which triggers the semiconducting property of the material. The semiconducting property can be switched off in the tune of nearly 16 times by heating the material at 80°C. This cycling has been verified by cycling the material about six times. Similar reversibility in the PL and DRS was also observed by cycling material about three times (Supporting Information, Table S3). The observed property can be attributed to the formation of a tetrameric aggregate that contains very strong interactions, such as cation–π, $COO^-\cdots H-N^+$ and $COO^-\cdots N^+$ interactions, and also the conjugated nature of BPCH. It is noteworthy that the small difference in the molecular structure of the one of the components was found to make huge differences in the crystal structure and therefore the property. For example, the use of a BPCP molecule, which contains cyclopentanone in place of cyclohexanone in BPCH, resulted in a non-photochromic material owing to the differences in the self-assembly process (see the Supporting Information). Previous examples contain either radical formations, which lead to photochromisim, or $\pi\cdots\pi$ charge transfer interactions, which lead to conductivity. As the present example contains both qualities along with cation–π and hydrogen-bonding interactions, leading to the exhibition of all three properties in one material. This novel supramolecular charge transfer material offers substantial potential for the development new generation of organic electronic and optoelectronic devices.

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