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Supramolecular Isomers

Distortional Supramolecular Isomers of Polyrotaxane Coordination Polymers: Photoreactivity and Sensing of Nitro Compounds[**]

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Abstract: *Distortional isomers, or bond-stretch isomers, differ only in the length of one or more bonds, which is due to crystallographic disorder in most cases. The term distortional isomerism is introduced to describe the structures of polyrotaxane 2D coordination polymers (CPs) that differ only by the relative positions in the neighboring entangled axles. A large ring and a long spacer ligand in 2D CPs yielded four different supramolecular isomers, of which two have an entangled polyrotaxane structure. One pair of C=C bonds in the spacer ligand is well-aligned in one isomer and undergoes [2+2] cycloaddition reaction, whereas the other isomer is photoinert. They also have different sensing efficiency for several aromatic nitro compounds. However, both isomers show selective PL quenching for the Brady's reagent. Structurally similar supramolecular isomers with different photochemical reactivity and sensing abilities appear to be unprecedented.*

Solid-state properties are dictated by the way in which the molecules are packed. It is well-known that a molecule can be crystallized in different structural arrangements (polymorphs) and thus they often have different morphologies, solubilities, color, melting or sublimation temperatures, densities, thermal or electrical conductivities, and other physical properties as well the chemical reactivities.[1] The study of polymorphism is important especially in pharmaceutical industries nowadays and also academically challenging one.[1a,2] On the other hand, in coordination polymers (CPs), the repeating building blocks are connected by the coordination bonds to furnish infinite arrays. In many cases, the same building blocks can be connected in different ways leading to different structures. The concept of isomerism in coordination complexes has been extended to CPs and called supramolecular isomerism by Zaworotko.[3] The examples for supramolecular isomer is growing in recent times but there are not many examples with distinct physical and chemical properties that characterize supramolecular isomers in CPs as polymorphs.[4]

Mechanically interlocked supramolecular structures such as rotaxanes are the well-known group of supramolecules, which are known for intriguing structures and have made impact with their potential applications in different fields.[5] The dynamic nature of wheel on the axial rod of the rotaxane structures has been used in molecular machines which can be controlled by various factors such as light, pH, and temperature.[5c,6] In contrast, the [2+2] photo-dimerization of organic molecules in these rotaxane structures is very rare, which might be due to the difficulties in attaining both the photoreactivity and the rotaxane formation simultaneously.[7]

Reversible structural changes in porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have potential applications in dynamic switching of the gas uptake, optical, electric, and magnetic properties.[8] In this regard, dynamic polyrotaxane MOFs have also been developed for this purpose.[5a,b,9] Such structures could result in the supramolecular isomers depending on the position of rotaxane wheel on the axial rod. To our surprise, such supramolecular isomeric structures are not encountered in polyrotaxane structures, to the best of our knowledge.

The photoluminescence (PL) properties of long delocalized organic spacer ligands can be enhanced by the metal cluster nodes by decreasing the non-irradiative decay and other transitions, such as MLCT and LMCT.[10] Owing to the comparably narrow PL band and porous nature, these compounds showed considerable selectivity for explosive nitro compounds, which are not only significant for security, but also for their high toxic nature as pollutants.[11] The detection of these molecules needs expensive equipment, such as gas chromatography, coupled with mass spectrometry, Raman spectroscopy, and other characterization methods that are not portable. Therefore, chemical sensors are considered to be the most reliable, inexpensive, and portable and highly demanding for the detection and sensing of selective molecules. Still there is much interest to discover new materials for selective sorption of different nitro compounds other than explosives.

Herein, we describe syntheses of four supramolecular isomers of $[Zn_2(bpeb)(sdb)_2]$ (**1**–**4**) based on 2D CPs from Zn^{II} salt, 1,4-bis[2-(4′-pyridyl)ethenyl]benzene (bpeb) and 4,4′-sulfonyldibenzoate (sdb) by varying the experimental conditions as shown in Figure 1. It is interesting to note that the intentional addition of water produced interpenetrated (**2**) and polyrotaxane (**3** and **4**) isomers. The large square formed between two angular space ligand sdb are connected by two $[Zn_2(O_2C{-}C)_4]$ paddle-wheels to form necklace-like 1D CPs that are further linked by the bpeb ligands through

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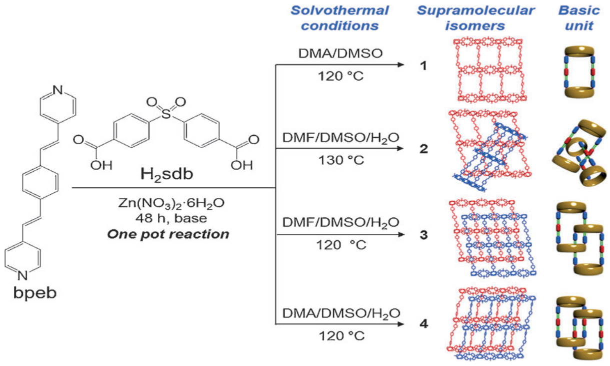

Figure 1. Synthesis of the supramolecular isomers **1**–**4** including the polyrotaxanes (**3** and **4**) and their structural comparison.[21]

the axial positions of Zn^{II} in the paddle-wheel building unit. Of these, one is a non-interpenetrating 2D sheet (**1**), while the second one is parallel/diagonal interpenetrating framework forming a 3D structure (**2**). The large [Zn$_2$(sdb)$_2$] square acts as a wheel and the long bpeb spacer from the neighboring 2D CP acts as an axle in forming two more isomers based on polyrotaxane motif (**3** and **4**; Figure 2). These two differ by the conformation of the bpeb as well as relative orientations of the axles in the twofold entanglements. In one entangled structure, the neighboring C=C bonds are found to be slip-stacked and undergoes single [2+2] cycloaddition reaction under UV light in a single-crystal-to-single-crystal (SCSC) manner. Otherwise the axle in the polyrotaxane structure appears to be dynamic when the solvents were removed by heat or solvent exchange as revealed by powder X-ray diffraction (PXRD) studies and photoreactivity. Interestingly, all of these compounds exhibit PL. Selective quenching of PL for **4** was observed for 2,4-dinitrophenylhydrazine (2,4-DNPH) compared to the other nitro analytes, and this selectivity has been also shown for the material obtained after the [2+2] cycloaddition reaction.

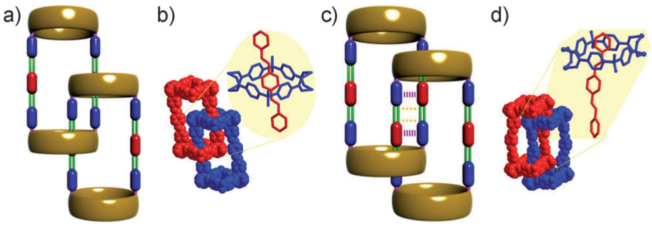

Figure 2. Structural comparison of polyrotaxanes **3** and **4**. Representation of the rotaxane units in a) **3** and c) **4**. The rotaxane units and the relative alignments of wheel and axle in b) **3** and d) **4**.

The structural differences between the polyrotaxane isomers **3** and **4** are briefly discussed herein. Notably, the position of rotaxane wheel on the axial rod in **3** and **4** are different; the distance between two entangled wheels in **3** is longer than that in **4** (Figure 1 and 2). The bpeb ligand in **4** has *trans–cis–trans* conformation (Figure 2 d), which is different from that in **3** (*trans–trans–trans*; Figure 2 b). This has reflected in the angular distortion of the bpeb ligand with respect to the [Zn$_2$(sdb)$_2$] square, which is 77.4° in **4** as compared to 81.1° in **3**. However, the length of the bpeb ligand (16.00 Å for **3** and **4**, N1···N2 distances) does not change despite the conformational changes (Supporting Information, Table S2). Supramolecular isomerism refers to two or more supramolecular systems that have the same composition and building blocks but generate different architectures.[3a,12] Both **3** and **4** have the same chemical composition with the exception of the guest molecules and have the same connectivity with small difference in the relative orientations of the bpeb ligands in the entangled polyrotaxane architectures. Thus, **3** and **4** may be considered as examples of distortional supramolecular isomerism. Furthermore, **3** and **4** can also be considered as conformational supramolecular isomers[1a,3] owing to different conformation of bpeb in **3** and **4** (Figure 2). Such conformational differences in bpeb ligand has been observed before in a guest-triggered reversible SCSC structural conversion between supramolecular isomers with unusual isomers of paddle-wheel building blocks.[13] Recently, an example for supramolecular isomerism in pseudo-polyrotaxane system containing a luminescent cuprous cyanide was reported by Zhang et al.[14] To the best of our knowledge, this is an unusual example of supramolecular isomerism in polyrotaxane structures by conformational differences of bpeb spacer ligand as well as relative distances between the bpeb ligands in the entangled structures.

A closer view of the twofold entanglement in **4** as shown in Figure 3 reveals that the bpeb pairs are aligned in a slip-stacked manner such that each phenylene ring is closer to a neighboring pyridyl group containing N2 atoms with centroid to centroid distance of 4.42 Å while the distance between the centers of the adjacent C=C bond pairs is 4.29 Å. The out-of-phase arrangement of the adjacent bpeb spacer ligand is congenial for photochemical dimerization by a [2+2] cycloaddition reaction. It is obvious from Figure 3 that such a single cycloaddition reaction will furnish a cyclobutane-based organic dimer that would result in another 2D polyrotaxane structure. The other neighboring pyridyl group containing N1 atoms is stabilized by weak face-to-face π–π interaction with phenylene rings of sdb ligand in [Zn$_2$sdb$_2$] square (Figure 3).

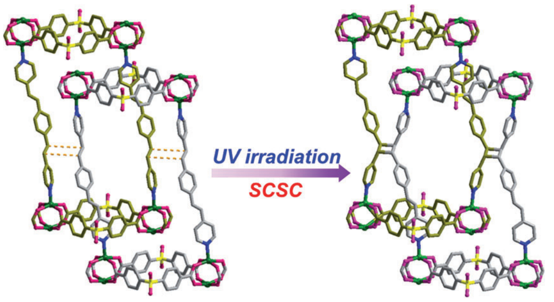

Figure 3. The SCSC transformation of polyrotaxane **4** to polyrotaxane **5** through the [2+2] photo-cycloaddition reaction.

The ^{1}H NMR spectrum of the solid obtained after irradiating **4** under UV light for 48 h dissolved in

$[D_6]$DMSO with the help of a drop of HNO_3 showed the appearance of cyclobutane peaks at 5.01 ppm along with other peaks owing to aromatic protons in the region 8.7–8.8 ppm and 7.7–8.0 ppm (Supporting Information, Figures S12, S13). Therefore, for better understanding of the final structure of this photo-irradiated product of **4**, we attempted to get single crystals of the product at the end of the cycloaddition reaction and succeeded.

The single-crystal X-ray crystallographic analysis of $[Zn_2(\textit{rctt}\text{-bpbpvpcb})_{0.5}(sdb)_2]\cdot 2\,DMA\cdot 2\,H_2O$ (**5**) (bpbpvpcb = 1,3-bis(4-pyridyl)-2,4-bis[4-(2-(4-pyridyl)-vinyl)phenyl]cyclobutane; Supporting Information, Figure S25) confirmed the quantitative photo-cycloaddition of bpeb with *trans–cis–trans* conformation (Figure 4). The space group $P\bar{1}$ was retained and the asymmetric unit contains the formula of the unit cell. The formation of bpbpvpcb from single cycloaddition of adjacent bpdb pairs caused distortions to the coordination sphere of Zn^{II} atom and overall 2D structure. Furthermore, the pyridyl ring with N1 atom of the bpbpvpcb is disordered over two sites with occupancy ratio of approximately 56:44. Previously a similar out of phase single photo-cycloaddition reaction has been observed, between bpeb pairs with a *trans–trans–trans* conformation.[15]

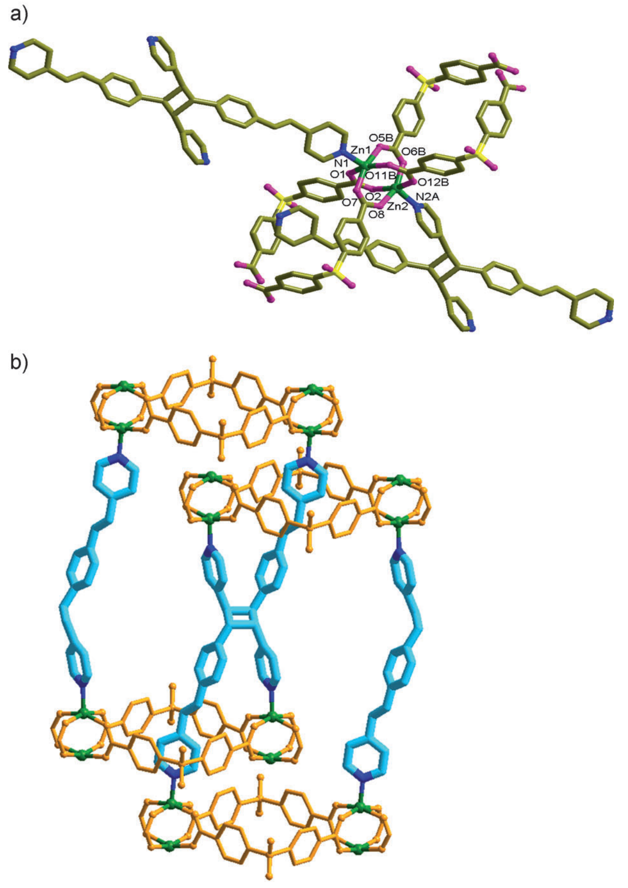

Figure 4. Crystal structure of **5**, $[Zn_2(\textit{rctt}\text{-bpbpvpcb})_{0.5}(sdb)_2]\cdot 2\,DMA\cdot 2\,H_2O$. a) A view showing the SBU and bpbpvpcb. Symmetry codes: (A): $1+x$, y, $-1+z$; (B): x, $1+y$, z. b) Rotaxane units with dimerized pillar ligands.[21]

The original two-fold entangled (4,4) net structure in **4** is transformed under UV light to a non-interpenetrated structure **5**, in an SCSC manner due to the formation of cyclobutane rings between the adjacent C=C bonds. The total potential solvent area volume is 885.6 Å^3, which is 31.1% of the unit cell volume.

Owing to the structural similarity, attempts have been made to transform **4** into **3** and vice-versa by soaking the single crystals in different solvents, but unfortunately they do not retain the single-crystal nature in this process. The PXRD experiments revealed new patterns obtained after soaking the single crystals of **4** in methanol (**4a**), for example. Interestingly, the PXRD patterns obtained for the sample after desolvation of **4** by heating matched with those of **4a** (Supporting Information, Figures S19, S20). However, **4a** is photostable under UV light. Therefore, it is likely that either the slippage of the bpeb ligands relative to each other in the entangled structure or their conformation changed in the desolvated compound **4a** and responsible for its photoinertness. On the other hand, formations of new covalent bonds in **5** during the [2+2] cycloaddition act as a clip to prevent this sliding[8a] and resulted in the formation of a highly rigid polyrotaxane structure. Therefore, herein we have shown for the first time the transformation of a flexible CP to a rigid CP using [2+2] photo-cycloaddition.

The strong luminescence nature of these compounds encouraged us to study the possible detection of organic molecules.[11,16] For this purpose, **3** was ground and dispersed in dimethylformamide (DMF). Upon excitation of this dispersed solution at 360 nm, a strong blue color emission has been observed with PL emission at 440 nm and 463 nm along with a small shoulder at 524 nm (Supporting Information, Figure S27).

To observe the guest-induced PL properties with the small aromatic compounds including nitrobenzene derivatives, we prepared different analyte solutions with 1 mM concentration and added to the dispersed solution of each framework compound with 1 mg in 1 mL of DMF.[11d] In the presence of 2,4-dinitrophenylhydrazine (so called Brady's reagent; 2,4-DNPH), for example, **4** showed the highest PL quenching up to about one seventh of the initial fluorescence intensity in 90 μM (17.8 ppm) solution (Figure 5).[17] For **3**–**5**, some nitrobenzene derivatives showed significant PL quenching, while the organic guests such as toluene, xylene, nitrobenzene, and some others showed no meaningful changes on the PL intensity (Figure 6).

Apart from wheel-axle distortion, **3** and **4** have similar structures and packing arrangements; the PL peaks of **4** blue-shifted relative to **3** with maxima occur at 420 and 433 nm as well as a small shoulder at 397 nm (Supporting Information, Figure S27). This suggests that there are significant fluorescent transitions between the ligands depending on their position (inter-ligand charge transition, LLCT).[18] The PL titrations have been performed on **4** which also showed selective PL quenching by 2,4-DNPH compared to other analytes. Moreover, **4** shows better quenching of fluorescence up to about one twenty-third of its initial PL intensity (Figure 5 and 6) as compared to **3**. Furthermore, we could even observe the PL quenching up to the concentration of

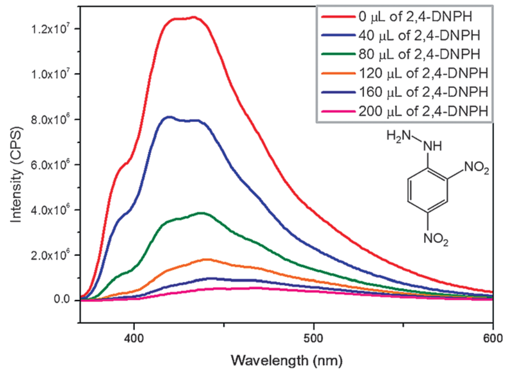

Figure 5. PL spectral changes in **4** (1 mg dispersed in 1 mL DMF) in the presence of 2,4-DNPH (0–200 µM, excitation at 360 nm).

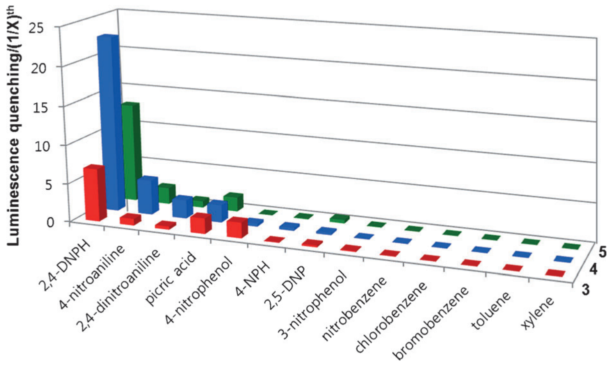

Figure 6. PL quenching efficiencies ($I_o/I-1$) obtained from different analytes by **3** (red), **4** (blue), and **5** (green) at room temperature.

5 µM (ca. 1 ppm) using **4** (Supporting Information, Figure S44).

To find the influence of the modified pillar ligand after the cycloaddition of **4**, we conducted the quenching experiments with **5**. Despite the disruption of π-electron cloud during the photoreaction of bpeb, a red-shift in the fluorescent peaks occurs relative to **4** with PL maxima at 440 and 453 nm as well as a shoulder at 482 nm (Supporting Information, Figure S27). This suggests that the fluorescence has been generated not only due to the inter-ligand charge transitions, but also due to LMCT, which is well known in MOFs.[11a,18] Moreover, bpeb and sdb ligands showed little fluorescence (Supporting Information, Figure S53), and the red shift of the PL peaks after the photoreaction of bpeb in **4** ruled out the possibility of ligand-centered fluorescence in these compounds. To our surprise, **5** also showed similar quenching properties as **4**, with best selectivity with 2,4-DNPH with PL quenching up to about one thirteenth of its initial intensity and followed by 4-nitroanilne, picric acid with more than half of its intensity, and all other analytes show very low quenching property with **5**. On the whole, **4** showed the best selective quenching with 2,4-DNPH up to the twenty-third part of initial intensity for 2,4-DNPH compared other nitro derivatives, and the stability of **3** and **4** of framework has been confirmed by the comparative PXRD and PL measurements before and after soakings in the aqueous solution of picric acid (1 mM) for 24 h (Supporting Information, Figures S54–S59).[11c]

As there is no significant pore which could accommodate the analytes in the framework, UV/Vis absorption spectra of all these analytes has been measured (Supporting Information, Figure S51) to understand the possible quenching mechanism.[11a–d] Among all of these compounds, 2,4-DNPH, 4-nitroaniline, 4-nitrophenylhydrazine, 2,5-dinitrophenol, and 2,4-dinitroaniline showed significant absorption bands at the excitation wavelength (Supporting Information, Figure S51). Therefore, this fluorescence quenching or the variation in the luminescence change of the framework might be due to the competition of absorption of excitation radiation from the source between analytes and the framework. The analytes filter the light absorbed by framework and subsequently quenches the luminescence.[19] However, we could not observe such a significant quenching with the other molecules that have absorption maxima at the excited wavelength, so we considered that there should be other possibilities for this quenching mechanism along with the filtration of excitation radiation. So we considered the other possible mechanisms such as redox activity of these nitro aromatic compounds with the framework. To evaluate this, we studied the quenching property of benzoquinone owing to its high reduction potential (Supporting Information, Figure S43).[20] In contrast to our hypothesis, the PL intensity has been enhanced with benzoquinone, which ruled out the possibility of redox activity of the fluorescent framework with the analytes. Therefore, we strongly suggest that there is a significant contribution from the resonant energy transfer between these analytes and framework owing to the proper match of electronic bands of framework with the analytes (Supporting Information, Figure S52), which would lead to the significant fluorescence quenching along with other possible mechanisms.[11a–d,18]

In summary, 2D CPs [$Zn_2(bpeb)(sdb)_2$], having large rings and long spacer ligands, yielded four different supramolecular isomers including a simple 2D sheet structure (**1**), an inclined two-fold interpenetrated 3D structure (**2**) and two two-fold entangled polyrotaxane structures **3** and **4** by varying the experimental conditions during the synthesis. The last two structures differ in the conformation (*trans–trans–trans* versus *trans–cis–trans*) and relative (slip-stacked) dispositions of the bpeb ligands and termed as distortional supramolecular isomers. Compound **3** is photoinert while one C=C bond pair between the offset bpeb ligand pairs in **4** has been aligned parallel and separated by 4.29 Å, and **4** undergoes SCSC structural conversion yielding another 2D polyrotaxane structure **5**. Sliding of bpeb linkers relative to each other occurs in **4** when the solvent was removed either by heating or exchanging with methanol to give another intermediate structure, which is also presumed to be another supramolecular isomer. The dynamic bpeb axles in the polyrotaxane structure were locked under UV light to a stable structure **5** through the formation of cyclobutane ring. All these compounds exhibit blue emission in the region 458–473 nm when excited at 360 nm. Compounds **3**–**5** were tested for sensing a number of nitro compounds, and all of these compounds show selective PL quenching for 2,4-DNPH compared to other nitro derivatives. This is the first time that structurally similar supramolecular isomers exhibit different photochemical reactivity and different sensing efficiencies.

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[21] CCDC 974666, 974667, 974668, 974669, and 975273 (compounds **1** – **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.