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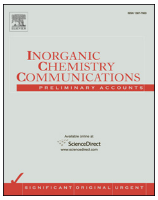

Short communication

A luminescent zinc coordination complex cocrystallized with benzenetetracarboxylic acid showing photoinduced coloration from grey to orange

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ABSTRACT

Tailoring photoinduced color of a donor-acceptor molecular system is achieved by introducing the macrocycle electron-deficient ligand into the structure of a zinc phosphate binuclear unit. Fluorescence quenching occurs accompanying with the light irradiation process due to energy transfer between the photoactive components.

Photochromic and photocolored complexes have attracted immense interest for their intrinsically attractive properties that have already led to real applications in optoelectronic devices, optical filters and optical memory [1,2]. Over the past decades, many photoinduced color transformation systems are explored involving the bond cleavage and reformation of the C—O bond [3], the reversible photocyclization [4], trans–cis isomerization [5], intramolecular proton transfer [6], and the intermolecular charge transfer (CT) process [7]. Among them, photoactive CT complexes are a kind of molecular switches based on the CT transfer process [8]. They are constructed by the suitable combination of electron deficient (acceptor) and electron rich (donor) components [9–10]. Under light stimuli, photoinduced electron transfer reaction takes place between the donor and acceptor groups accompanying a photocoloration process [11–13]. By comparison with the syntheses of previous organic photosensitive compounds, photoactive materials created in the CT mode avoid inconvenient organic synthesis process and provide more chances for the structural design [14]. Recently, the development of photosensitive materials based on metal–ligand complexes emerges as an efficient way to build new CT photoresponsive molecular systems [15–17]. The photoactive characters of these complexes can be perturbed and tuned by the combination of different metal centers and ligands [18–21]. Although CT photoactive complexes showing photoinduced coloration from yellow to blue [22], yellow to black [23] and yellow to red [24] have been well reported, the preparation of donor–acceptor material with new color response range is still a critical need to be further explored for the development of optical switches. Herein, we report the preparation and photosensitive properties of an interesting photoactive zinc coordination molecule $[Zn(HPO_4)(PYTPY)]_2 \cdot (H_4BTEC)_2 \cdot (H_2O)$ **1** (PYTPY = 4′-(4-pyridyl)-2,2′:6′,2′′-terpyridine, H_4BTEC = 1,2,4,5-benzenetetracarboxylic acid). In its hydrogen-bonded aggregate structure, the binuclear $[Zn(HPO_4)(PYTPY)]_2$ unit is surrounded by six H_4BTEC molecules locating at the center of the molecular cage. The aromatic *N*-heterocyclic component and its electron-deficient character make the grafted pendant group PYTPY act as light sensitizer and electron acceptor [25]. Upon irradiation with light, the process of electron transfer from H_4BTEC to PYTPY is associated with the process of inter-ligand energy transfer from PYTPY to H_4BTEC. The coupling of these procedures creates a fluorescent-photocolored bifunctional molecular system. Distance, orientation and interactions, packing mode and the assembly units are important factors in affecting the photoresponding behaviours of donor-acceptor materials. Accompanying the quenching of fluorescence, it is observed that the grey crystals of **1** gradually turn orange with the formation of stable radicals. This designed donor-acceptor molecular system presents a new color response range with increasing UV absorption at 490 nm under light stimuli.

Grey crystals of complex **1** are obtained by a hydrothermal reaction of $ZnBr_2$, PYTPY, H_4BTEC and H_3PO_4 in 10 mL water with a molar ratio of

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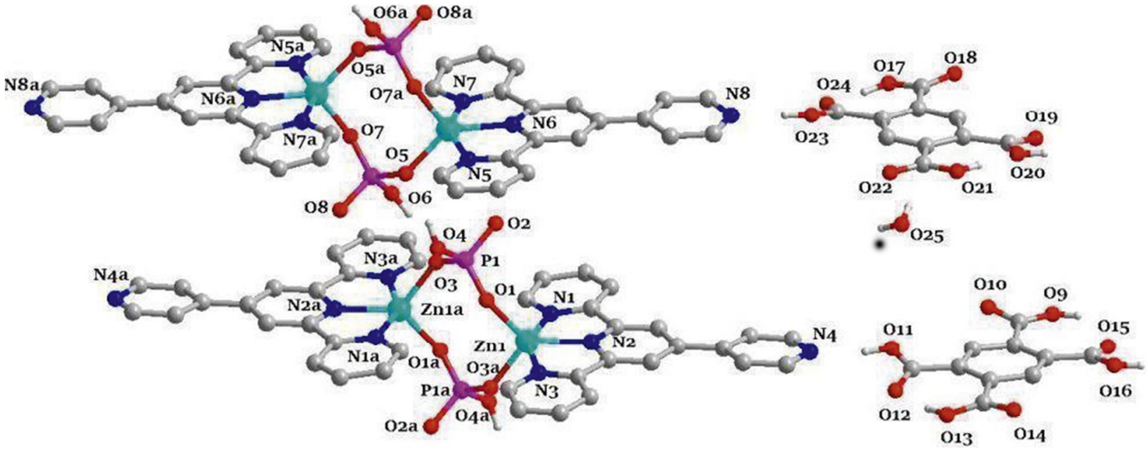

Fig. 1. Molecular structure of complex **1**.

2:1:5:47 at 140 °C [26]. Phase purity of the as-synthesized bulky sample was verified by the powder X-ray diffraction (PXRD) data (Fig. S1, see SI). X-ray crystal diffraction analysis reveals that it contains a two dimensional hydrogen-bonded network with $[Zn(HPO_4)(PYTPY)]_{2,}$ H_4BTEC and crystalline water as building units [27]. The Zn^{2+} center is five-coordinated with three nitrogen atoms from a chelating PYTPY ligand, two oxygen atoms from two $HPO4^{2-}$ anions (Fig. 1). The H_4BTEC molecule is hydrogen bonded in the O—H···N manner with the neighbour PYTPY group (O23···N8 = 2.570(2) Å, O11···N4 = 2.621(1) Å). One water molecule is included into the lattice and forms hydrogen-bonding with the H_4BTEC unit (O22···O25 = 2.958(3) Å). Each $[Zn(HPO_4)(PYTPY)]_2$ unit is surrounded by six H_4BTEC molecules locating at the center of the molecular cage (Fig. 2). The ring systems of PYTPY show a close stacking feature over the rings of adjacent H_4BTEC units in a face-to-face mode with a centroid···centroid of 3.696(3) Å. These structural features satisfy the requirement for an intermolecular electron transfer [29]. Electron-deficient characters of N-substituted heterocyclic organic molecules make them well-known as electron acceptors [7,22]. A typical photosensitive donor-acceptor molecular system can be constructed while the PYTPY ligand is combined with electron rich carboxylate component via the formation of a supramolecular close-packed structure.

Upon exposure to light irradiation (xenon lamp, 150 W), complex **1** shows crystalline photocoloration from grey to orange (Fig. 3). UV–vis spectrum of the grey crystal shows absorption bands at 355 nm and 445 nm, which relate to the π–π* and n–π* transitions of the aromatic rings. After irradiation, a new broad absorption band at 490 nm emerges for the orange crystal, and it increases with extending the irradiation time. ESR data (g = 2.0037, Fig. 4) indicate that the outer-irradiated process is accompanied by the generation of organic radicals. The combining donor and acceptor units and the structure of assembly motif all are important factors to modify the color response range of a photoinduced electron transfer (PET) molecular system. Different from reported metal-viologen complexes mostly showing photo-coloration from yellow to blue, the D-A system of **1** exhibits a new color response from grey to orange. The control of supramolecular assembly via selecting electro-deficient PYTPY (acceptor: *N*-heterocycle) and electro-rich H_4BTEC (donor: carboxyl group) as base units is a useful approach to build new interesting photoactive supramolecular aggregates. Complex **1** shows maximum fluorescent emission at 450 nm with 360 nm light excitation, which is assigned to luminescence of the PYTPY component (Fig. 5). The same as previous fluorescent-photocoloration molecular switches based on metal-viologen complexes, the fluorescent intensity of **1** decreases with the time of irradiation. These results are attributed to energy transfer from a fluorophore to a photocoloration group in a dyad system [30]. The fluorescent emission of the PYTPY ligand is well overlapped with the absorption band of the photocoloration components. Kinetic calculation results indicate that the photocoloration process of complex **1** is coupled with a reversible fluorescence change. The increase in UV absorption is proportional

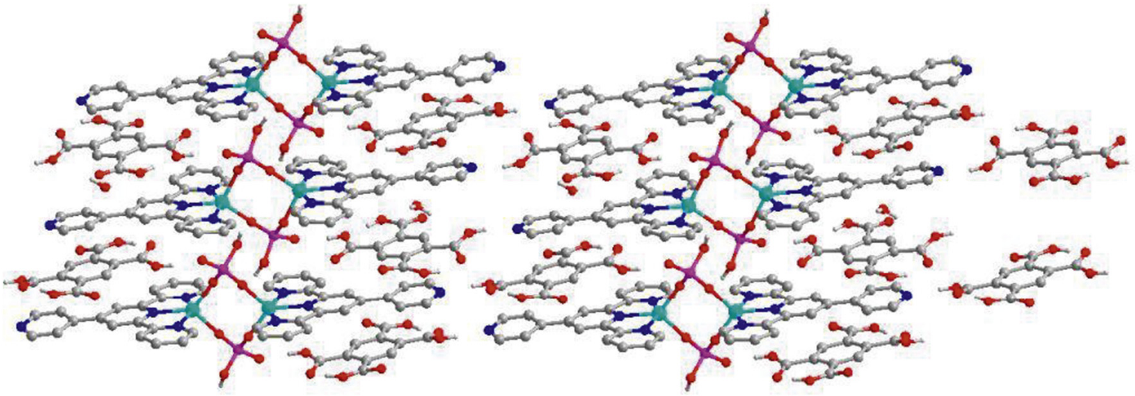

Fig. 2. Packing diagram of complex **1** to show the contact patterns between the fragments.