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A photochromic naphthalene diimide coordination network sensitized by polyoxometalates†

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Metal-ion-directed assembly of naphthalene diimide tectons cooperatively enhanced by anion–π interactions of giant anions, $PMo_{12}O_{40}^{3-}$, leads to a novel organic–inorganic hybrid with ultra-fast-responsive photochromic properties, which is attributed to the polyoxometalate-sensitized photo-induced radical generation of naphthalene diimide units.

Photochromic materials, *i.e.*, compounds that undergo a light-induced reversible color change, have received much attention due to their potential applications in many fields such as protection, decoration, optical switching, memory, filters, displays, modulators, *etc.*[1] The research on this domain is mainly concentrated on pure organic[2] and inorganic photochromic compounds,[3] while recently more and more attention has been drawn to the development of photochromic inorganic–organic hybrids not only because of the opportunity to combine the distinctive properties of both inorganic and organic components in one material but also the possibility of producing novel properties by the synergetic effects between two components. To our surprise, few examples exist of hybrids in which both inorganic and organic components are photoactive species.[4]

Naphthalene diimides[5] (NDIs) are an attractive class of electron-deficient dyes, which may undergo a reversible one-electron reduction to form stable radical anions in the presence of electron donors upon irradiation. This makes them an ideal chromophoric π-acceptor for the photochromic donor–acceptor composites. Polyoxometalates[6] (POMs) are a unique class of multi-functional anionic metal oxygen clusters that exhibit good redox and photo-activity, and can act as electron donors in photo-induced electron transfer processes.[7] Based on the electronic complementarity of NDIs and POMs, there is every reason to believe that two such photochromic species can be compounded into an inorganic–organic hybrid through less-studied anion–π interactions.[8] Herein, we report that this concept is indeed viable.

For the realization of this concept, we chose facile *N*,*N'*-di-(4-pyridyl)-1,4,5,8-naphthalene diimide[9] (DPNDI) anchoring two pyridine groups at both sides as a proof-of-concept organic component because it can interact with metal cations to form porous cationic coordination networks that will somewhat balance the anionic charges of inorganic photochromic polyoxometalates. A further reason is that the porous coordination networks will provide enough cavity space to encapsulate polyoxometalates and other guests for further applications. Moreover, recently we have demonstrated that coordination interactions can increase the π-acidity of DPNDI,[10] which is anticipated to enhance its anion–π interactions with polyoxometalate anions. For the polyoxometalates, saturated polyanions Keggin-type $PMo_{12}O_{40}^{3-}$ were used. As expected, the combination of DPNDIs with zinc fluorosilicate ($ZnSiF_6$) in the presence of giant anions, $PMo_{12}O_{40}^{3-}$, led to a hybrid of polyoxometalates and NDI coordination networks, in which each polyanion is stabilized by π-acceptors of DPNDI tectons through anion–π interactions. Interestingly, such anion–π interactions indeed have a cooperative effect on coordination interactions of DPNDIs. The optical property study reveals that the photochromic process of this hybrid originated from the photo-induced radical generation of DPNDI linkers, while the POMs mainly serve as photosensitizers to reinforce NDI radical generation.

In crystallization tubes, upon slow diffusion of an EtOH solution of $ZnSiF_6·6H_2O$ into an *N*-methylpyrrolidin-2-one (NMP) solution of DPNDI and $H_3PMo_{12}O_{40}$ with a buffered layer of a mixture solution of EtOH and NMP (1 : 1 in volume), yellow crystalline $[Zn_2(DPNDI)_2(NMP)_4(H_2O)_2F]·(PMo_{12}O_{40})$ (**1**) was obtained after several days. The combination was analyzed by the X-ray diffraction technique on single crystals, which revealed that it is a hybrid of polyanions and NDI based

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coordination networks. In the meantime, the purity of the generated solid phase was investigated by X-ray diffraction on powder samples (Fig. S3, ESI†), which revealed that its crystalline materials are in the pure phase *i.e.* matching observed and simulated peaks.

The structural analysis revealed that the crystal of **1** (monoclinic, *P*2/*c*) consisted of two-dimensional NDI based coordination networks and $PMo_{12}O_{40}^{3-}$ (Fig. 1). In these networks, each F^- anion bridges two octahedral zinc centres with different coordination environments to form a trivalent dinuclear complex (Fig. 1a), in which one zinc centre is saturated by four O atoms from four NMP molecules in the square plane and one O atom from water molecule in the opposite axial position (d_{Zn2-O} = 2.10–2.14 Å, d_{Zn2-F} = 1.99 Å), while the other is surrounded by four N atoms from four DPNDI units in the square plane and one O atom from water in the opposite axial position (d_{Zn1-N} = 2.13–2.16 Å, d_{Zn1-O} = 2.22 Å, d_{Zn1-F} = 2.00 Å). Then each formed dinuclear complex is interconnected by four DPNDI linkers to generate a cationic two-dimensional NDI coordination network ($d_{Zn1-Zn1}$ = 19.69 Å) with all the second zinc nuclei standing above the plane (Fig. 1b). For each DPNDI, the dihedral angle between the NDI core and the pyridine group is *ca.* 60.84°, which is slightly smaller than that of the free ligand (*ca.* 70.4°).[11] In the *ac* plane, a couple of face-to-face networks slipped around half distance of two neighboring zinc centers so that each of the two DPNDI units from two networks can sandwich one $PMo_{12}O_{40}^{3-}$ polyanion through anion–π ($d_{\pi-O}$ = 3.17–3.53 Å) and CH···anion interactions (d_{C-O} = 3.27–3.29 Å, Fig. 1c) affording an neutral sandwiched layer with a thickness of 12.78 Å (Fig. 1d and 1e). Finally along the *b* axis, the neighbouring two layers are further stacked end to end by π–π interactions of DPNDI units ($d_{\pi-\pi}$ = 3.47 Å, Fig. 1e). Undoubtedly, such compact packing between inorganic and organic photoactive moieties should play a very important role in their electron separation and transfer upon application of external stimuli.

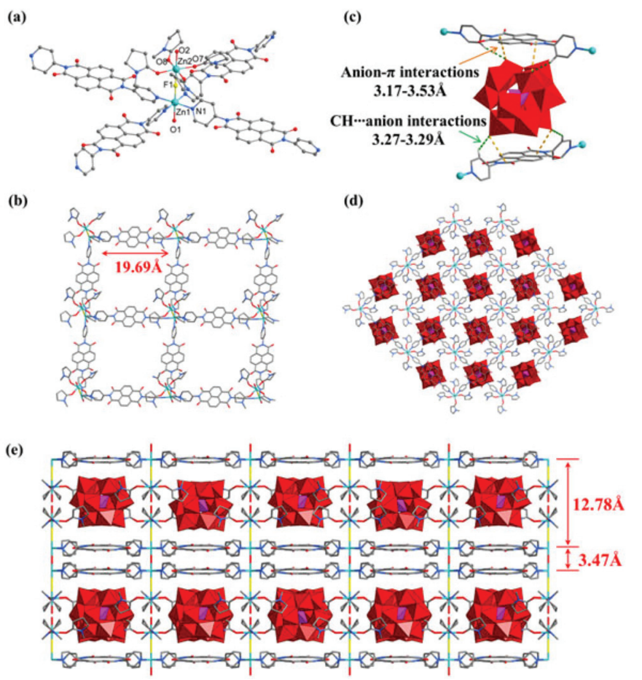

Fig. 1 (a) Coordination environment of Zn^{2+} in complex **1** (symmetry codes: 1 − *x*, *y*, 0.5 − *z*); (b) two-dimensional coordination network; (c) the interactions between NDI units and $PMo_{12}O_{40}^{3-}$ polyanion; (d–e) top and side views of the sandwiched layer of polyoxometalates and naphthalene diimide coordination networks. For clarity, all the H atoms except for those highlighting CH···anion interactions in (c) are omitted.

Recently we have reported a cooperative effect between lone pair-π and coordination interactions in the NDI based coordination networks.[10] Herein, a similar synergy between anion–π and coordination interactions can also be observed. In the sandwiched layers, the DPNDI units with shorter distances between polyoxometalate anions and π-acceptors (*ca.* 3.17 Å, while 3.53 Å for those of other kinds of DPNDI units) possess shorter distances with metal cations (*ca.* 2.13 Å, while 2.16 Å for those of other kinds of DPNDI units), indicating that their coordination abilities reinforce with the increasing anion–π interactions. Due to the electron-deficient nature, the electron densities at the N atoms of pyridine moieties in DPNDIs are very low, but it can be strengthened by the donating electrons from anions through anion–π interactions.

As expected, hybrid **1** is sensitive to sunlight and undergoes a photochromic transformation from yellow to dark green (crystal **2**) upon irradiation by sunlight or a 365 nm UV light (11 W) within one minute (Fig. 2a, inset). The crystal **2** is stable in air and can return to yellowish in a dark room for three days at ambient temperature. X-Ray crystallography and PXRD (Fig. S3†) revealed that the crystal structure of **2** is identical to **1**, but their UV/Vis spectra are different (Fig. 2a). This phenomenon indicates that the photo-responsive behaviours may be a result from an electron-transfer chemical process in

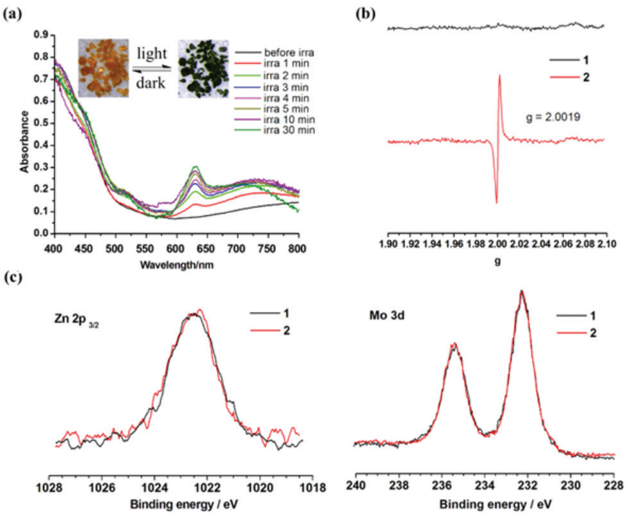

Fig. 2 (a) UV/Vis spectral changing of hybrid **1** upon irradiation by a 365 nm UV light (1, 2, 3, 4, 5, 10 and 30 minutes), the inset shows the photochromic effect of a single crystal from photographic images; (b) ESR spectra for **1** and **2**; (c) XPS core level spectra of Zn and Mo atoms in **1** and **2**.

the structure, and not from a structural transformation. As shown in Fig. 2a, the UV-Vis spectroscopy reveals that the major effect of the irradiation by a 365 nm UV light is not the enhanced absorptions in the regions 490–540 nm and 580–800 nm, but the appearance of an entirely new sharp band with an absorption maximum at 625 nm, whose intensity increases with the prolongation of irradiation time. According to the previous studies of NDI derivatives,[12] these spectral features are attributed to the formation of the radical NDI species, which is indeed substantiated by ESR studies (Fig. 2b). Hybrid **1** exhibits no ESR signal, but **2** shows a single-peak radical signal with a *g* value of 2.0019. No redox reaction occurs in $PMo_{12}O_{40}^{3-}$ polyanions and zinc centres, which is supported by X-ray photoelectron spectroscopy. As depicted in Fig. 2c, the core-level spectra show that the peak shapes and positions of zinc and molybdenum atoms in **1** and **2** are almost unchanged. Therefore, the photochromic behaviour of hybrid **1** originated from the photo-induced radical generation of DPNDI linkers, but not those of POMs or zinc nodes.

Compared to the photoresponsive rate of the reported NDI based photochromic coordination networks (a few minutes)[13] that of hybrid **1** increases significantly (within 1 minute), which may be attributed to the introduction of POMs. It is known that POMs are a unique class of photochromic clusters, which can accept one electron from the electron-donating solvents (*e.g.* NMP, *N*,*N*′-dimethylacetamide, *N*,*N*′-dimethylformamide) upon irradiation to undergo a metal-to-metal extra intervalence charge transfer.[6*a*,14] However, in our case, due to the presence of more electron-deficient and close-contacting DPNDI units, the electrons accepted by POMs from NMP molecules (the distance between POMs and NMP, d_{O-C} = 3.24–3.34 Å) will be transferred to DPNDI units quickly to form the respective NDI radicals. That is, POMs just serve as photosensitizers for the photo-induced radical generation of NDI moieties. Combining the photo-induced electron transfer pathway from NMP to DPNDI units directly, the photoresponsive rate of hybrid **1** is increased without a doubt. Moreover, it is worth pointing out that the compact π–π interactions are other non-negligible factors for the increased photoresponsive rate of hybrid **1** since face-to-face π–π interactions are known to play a crucial role in stabilizing the radical species in the hybrid.[15]

As stated above, the color of crystal **2** can return to that of **1** by standing in a dark room for three days at ambient temperature, which is supposed to be a scavenging process of NDI radicals by O_2 in air. Actually, a similar reversible behaviour but with quicker response (within 2 hours) can be observed upon UV irradiation of crystal **1** and addition of sodium nitrite aqueous solution (0.1 mmol L^{-1}) to crystal **2** (Fig. S4, ESI†). Importantly, such coloration and decoloration processes showed good reproducibility for many cycles, indicating that hybrid **1** may find application as an indicator for the trace nitrite in out-of-date foods.

In summary, we have demonstrated that the metal-ion-directed assembly of naphthalene diimide tectons under a synergistic effect of anion–π interactions from giant anions, $PMo_{12}O_{40}^{3-}$, resulted in a novel organic–inorganic hybrid, which exhibited an ultrafast-responsive photochromic property. Interestingly, such a photochromic process mainly originated from the photo-induced radical generation of naphthalene diimide units, while other photoactive polyoxometalates serve as photosensitizers to reinforce NDI radical generation. Further studies on similar systems with different photochromic properties are in progress.

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