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A method of synthesizing coordination nanofibers by extracting the structural motif of metal-organic frameworks (MOFs) is demonstrated. In these soluble nanofibers, multiple chromophores with largely different size and shape can be arranged at desired compositions, and excited triplet energy migrates among the densely assembled chromophore arrays, showing an efficient photon upconversion even at very low concentration.

The construction of supramolecular architectures with π-conjugated molecules by non-covalent interactions is important for obtaining unique optical properties and effective exciton transport.[1-7] The core to achieve these functions is the control of orientation and distance between neighbouring π-moieties. While there have been many examples of photofunctional supramolecular systems, it is still challenging to precisely control the arrangement of multiple chromophores when their molecular size and shape are largely different, and to keep the structural integrity even at low concentrations due to the dynamic nature of non-covalent bonds.

Here, we introduce a new coordination copolymerization approach to overcome these challenges, being inspired by the solid-state metal-organic framework (MOF) chemistry (Figure 1).[8-10] In MOF structures, bridging ligands are positioned with highly controlled orientation and distance, allowing effective electronic coupling and energy transfer among chromophoric ligands.[11-14] Instead of the rigid bridging ligands employed in MOFs, we introduced alkyl chain-modified lipophilic ligands to prepare soluble coordination nanofibers (Fig. 1). The conversion of solid-state metal complexes to soluble coordination polymers allows us to achieve self-assembly of one-dimensional chains in solution.[2, 15] This approach is expected to further provide a means for arranging multiple chromophores with different size/shape at desired compositions, which has been difficult to achieve with the solid-state coordination chemistry.

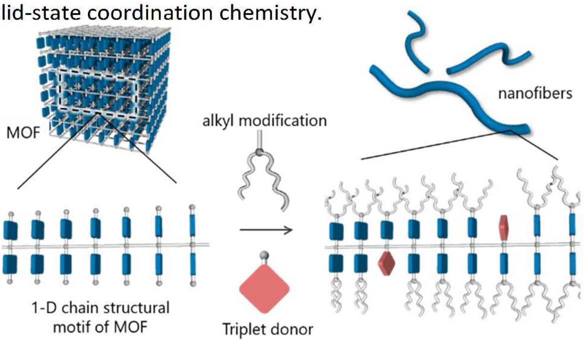

Fig. 1 Conceptual illustration of translating structural motifs of solid MOFs into soluble coordination nanofibers with lipophilic ligands.

To prove the concept, we shed light on photon upconversion based on triplet-triplet annihilation (TTA-UC). TTA-UC converts lower-energy photons into higher-energy photons, offering the promising potential in solar energy harvesting and high-resolution imaging.[16-31] In the typical TTA-UC scheme, the donor (sensitizer)-to-acceptor (emitter) triplet-triplet energy transfer (TTET) and succeeding inter-acceptor TTA through electron-exchange Dexter mechanism result in upconverted emission from acceptor excited singlets (Fig. S1, ESI†). In order to achieve a highly efficient TTA-UC in molecular assemblies, there are several conditions to be satisfied.[25] First, inter-acceptor distance should be within 1 nm for effective triplet energy migration among acceptor arrays. Second, it is necessary to avoid excessive interactions between neighbouring acceptors that cause concentration quenching of the fluorescence. Third, donor molecules are homogeneously doped without aggregation in acceptor arrays for efficient TTET.[18] To satisfy these requirements, we designed

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coordination polymers by referring the prototypical MOF called MIL-53, in which Al^{3+} ions are coordinated with benzene-1,4-dicarboxylate (BDC) and bridging hydroxyl (μ_2-OH) ligands to form the one-dimensional (1D) chain structure (Fig. 2a).[32] The distance between neighbouring BDC ligands of 0.66 nm is appropriate for inter-acceptor Dexter energy transfer without concentration quenching. A porphyrin donor (**Por**) and an anthracene acceptor (**An**) having a carboxylate group were complexed with Al^{3+} ions to form 1D lipophilic coordination copolymers (Fig. 2b). An efficient triplet energy transfer from **Por** to **An** as well as an effective migration of triplet excitons among the **An** ligands lead to an efficient upconverted emission. Interestingly, the efficient TTA-UC was maintained at a very low copolymer concentration, demonstrating the structural integrity of the diluted nanofibers due to the strong Al-O coordination bonds.[33]

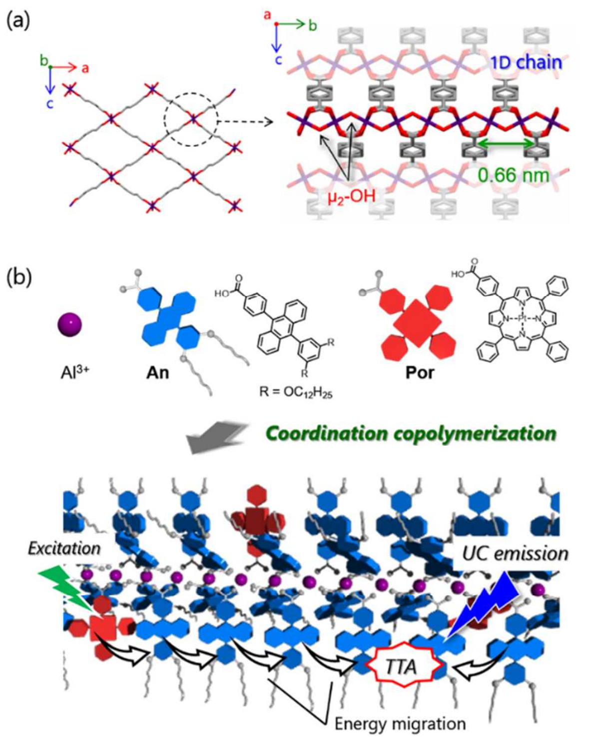

Fig. 2 (a) Crystal structure of MIL-53.[32] C, grey; O, red; Al, purple. Hydrogen atoms are omitted for clarity. (b) Chemical structures of **An** and **Por,** and schematic illustration of TTA-UC in the coordination copolymers Al-**An**-**Por**.

We first synthesized and characterized a coordination homopolymer Al-**An** by complexation between Al(III) ions and lipophilic **An** ligands. The synthesis of asymmetric **An** molecules was conducted by stepwise Suzuki-Miyaura coupling reactions (Scheme S1, ESI†). The homopolymer Al-**An** was synthesized in a high yield from **An**, $Al(NO_3)_3 \cdot 9H_2O$ and trimethylamine in N,N-dimethylformamide (DMF) by using microwave heating (see ESI† for details). In the reaction product, a FT-IR peak due to carboxylic acid moieties at around 1700 cm^{-1} disappeared, and new peaks assignable to asymmetric and symmetric vibrations of carboxylate groups appeared at 1595 cm^{-1} and 1432 cm^{-1}, respectively (Fig. S2, ESI†). This result indicates the formation of coordination bonds between Al^{3+} ions and **An** ligands.[32] The stretching and deformation vibrations of the μ_2-OH group were found as peaks at 3690 cm^{-1} and 980 cm^{-1}, respectively. Elementary analysis of the product showed a good agreement with the calculated chemical formula of $[Al(\mathbf{An})_2(OH)]_n$, and this composition is consistent with the model MIL-53 structure.[32] The synthesized Al-**An** showed a high solubility in low-polarity organic solvents such as chloroform, toluene and methylcyclohexane due to the presence of alkyl chains surrounding the coordination polymers.

To obtain the structural information of Al-**An** in solution, we carried out high-speed atomic force microscopy (HS-AFM) measurements which enable to directly observe assembly structures even in solution. When the methylcyclohexane solution of Al-**An** was placed on highly ordered pyrolytic graphite (HOPG) substrates, developed nanofibers were clearly observed in HS-AFM (Fig. 3a). The cross-sectional analysis shows that the height of nanofibers is about 3 nm, which is in agreement with the width of a single one-dimensional chain structure obtained by molecular modeling (Fig. 3b). While it is known that Al-oxo clusters with different size and structure exist, large area scans of HS-AFM showed only nanofibers with uniform thickness, confirming the one-dimensional chain structure of corner-sharing AlO_6-octahedra (Fig. S3). To our surprise, the Al-**An** nanofibers showed dynamic conformational changes within a few seconds, revealing the unique flexibility of the isolated coordination polymers in solution (Fig. 3c, Supplementary Movies). Apparently, physical property of the isolated one-dimensional coordination chains in solution is distinct from that of the bulk MOFs, where the rigid nature is offered by three-dimensional structural integrities. The absence of crystallinity in the coordination chains is supported by

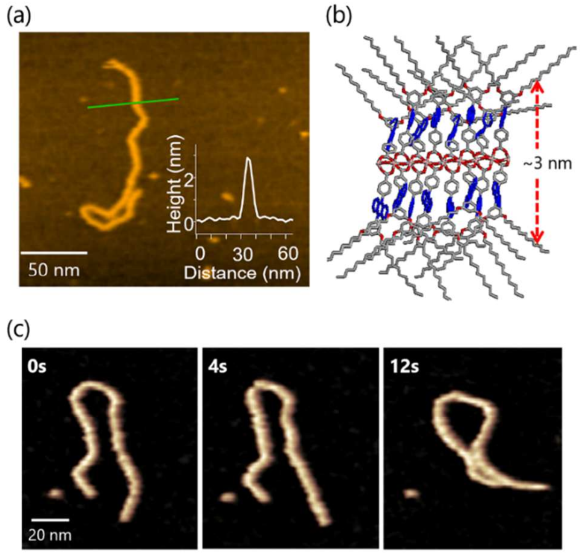

Fig. 3 (a) HS-AFM topographic image of Al-**An** in methylcyclohexane on HOPG substrates. Inset; AFM cross-sectional profile along the green line. (b)

Molecular structure of Al-**An** estimated using Spar-tan'14 software. (c) HS-AFM snap shots of Al-**An** in methylcyclohenane on HOPG substrates at different times (scan area is 80 x 47 nm^2).

powder X-ray diffraction (PXRD) measurements of Al-**An** cast films that showed no distinct peaks at the high-angle region (Fig. S4, ESI†). On the other hands, a PXRD peak was observed at 2.6° (d = 3.4 nm) that may correspond to the inter-chain distance as expected from the HS-AFM results.

We carried out optical characterizations of Al-**An** homopolymers to get more insight into the inter-chromophore arrangement. Fig. S5 in ESI† shows steady-state absorption and emission spectra of Al-**An** homopolymers (25 μM) and those of monomeric **An** ligand (25 μM) in methylcyclohexane. The concentration of Al-**An** is based on the ligand **An** concentration. The ^1B_b absorption band of the anthracene chromophore in **An** is observed at around 260 nm. Meanwhile, the polymer Al-**An** showed a blue-shifted peak at 250 nm and a red-shifted shoulder at around 265 nm. The transition moment for the ^1B_b band is parallel to the long-axis of anthracene chromophore, and the observed spectral change implies the exciton coupling among obliquely aligned chromophores around the one-dimensional chains of Al-**An**.[34] Slight red shifts and broadening were also observed in the ^1L_a absorption band at 330-400 nm upon complexation. The emission spectra of Al-**An** also showed a slight red shift (~3 nm) in comparison with the **An** ligand (Fig. S5, ESI†). Importantly, both of Al-**An** and **An** showed single-exponential fluorescence decays (Fig. S6, ESI†). The fluorescence quantum yield of Al-**An** was as high as 66%, similar to 70% observed for monomeric **An**. Consequently, only minor changes were observed in radiative (k_r) and nonradiative (k_{nr}) decay rates of the S_1 state by complexation with Al ions (Table S1, ESI†). It is noteworthy that no significant concentration quenching was observed in the polymeric Al-**An**. This is consistent with the moderate inter-ligand distance of 0.66 nm in the model MIL-53 structure (Fig. 2a). We stress that this inter-ligand distance is sufficient to avoid the concentration quenching but is close enough for triplet energy transfer as demonstrated below.

To prepare upconverting nanofibers, carboxylate-modified Pt(II) tetraphenylporphyrin (**Por**) was newly synthesized as a triplet sensitizer (Scheme S2, ESI†). The coordination copolymers Al-**An**-**Por** were obtained as red powder by the similar preparation scheme for Al-**An** in the presence of **Por**. The molar ratio of [**Por**]/[**An**] was estimated by UV-vis measurement. We found high tunability of the molar ratio in Al-**An**-**Por** copolymers by varying the feed concentration of **Por** in the synthesis (Fig. S7, ESI†). The Q band of monomeric **Por** in toluene was observed at 511 and 539 nm, which exhibited red shifts to 516 and 541 nm in its bulk specimen due to aggregation (Fig. S8, ESI†). Significantly, Al-**An**-**Por** showed similar spectrum as compared with free **Por** in solution. Therefore, the current coordination copolymerization approach allows homogeneous distribution of **Por** in the coordination copolymers without segregation despite the considerably different size and shape of the two chromophores (Fig. 2b).

We evaluated TTA-UC properties of Al-**An**-**Por** ([Al-**An**-**Por**] = 4 mM in which [**Por**] = 8 μM) in deaerated toluene. The concentration of Al-**An**-**Por** is based on the ligand **An** concentration. We used toluene instead of methylcyclohexane as a solvent for TTA-UC measurements since an upconverted emission in methylcyclohexane was observed but not stable at high excitation intensity probably due to local heating associated with the high viscosity of the solution. The deaerated solutions were prepared in an Ar-filled glove box ([O_2] < 0.1 ppm). Under excitation at 532 nm, an upconverted blue emission was observed at around 440 nm (Fig. 4a). Importantly, the phosphorescence of **Por** at around 670 nm was not detected, demonstrating a nearly 100% triplet energy transfer from **Por** to **An** which are co-facially arranged in coordination copolymers.[31] The blue UC emission was clearly observed by naked eyes without using any filters (Fig. 4a).

The observed upconverted emission is based on the TTA process, as confined by lifetime measurements and excitation intensity dependence. The toluene solution of Al-**An**-**Por** showed a ms-scale delayed fluorescence upon pulsed excitation at 531 nm (Fig. S9a, ESI†). This result supports that the UC emission is mediated by long-lived acceptor triplets. The lifetime of triplet excited state (τ_T) in Al-**An**-**Por** was estimated as 2.1 ms.[35] The TTA-based UC emission intensity generally shows the quadratic incident light intensity dependence at low excitation intensity regime, which turns into the first-order dependence by increasing the excitation intensity.[36-38] A double logarithmic plot for the UC emission intensity of Al-**An**-**Por** as a function of incident light intensity showed a transition from slope of 2 to 1, providing the further evidence for the TTA-based mechanism (Fig. S9b, ESI†).

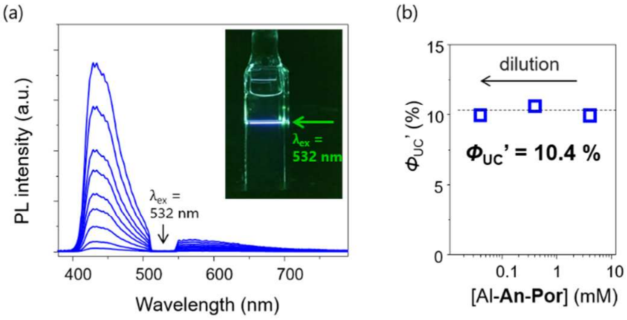

Fig. 4 (a) PL spectra of Al-**An**-**Por** ([Al-**An**-**Por**] = 4 mM in which [**Por**] = 8 μM) in deaerated toluene with various excitation intensities from 0.5 W cm^{-2} to 10 W cm^{-2} (λ_{ex} = 532 nm, 532 nm notch filter). A photograph under 532 nm green laser excitation without using any filter. (b) UC efficiency (Φ_{UC}') with different Al-**An**-**Por** concentrations in deaerated toluene (λ_{ex} = 515 nm).

We confirmed that the TTA-UC events take place within each single chains of Al-**An**-**Por**. When a mixed toluene solution of **An** and **Por** without Al(III) ions was frozen at 77K, no UC emission was observed (Fig. S10, ESI†). This is because TTET and TTA processes are based on Dexter energy transfer between molecules in close contact (< 1 nm),[36] which do not happen in the frozen molecularly dispersed solution. In stark contrast, the UC emission of Al-**An**-**Por** in toluene was clearly observed even at 77K (Fig. S10, ESI†).[25] These results indicate that triplet excited states, generated by the Dexter energy transfer from **Por** to **An**, can migrate along the dense **An** arrays in the polymeric structure without the help of molecular diffusion.

Thanks to the efficient donor-to-acceptor TTET and high fluorescence quantum yield, Al-**An**-**Por** showed a high UC efficiency (Φ_{UC}') of about 10 % in deaerated toluene at room temperature, which is comparable to previous efficient triplet energy migration-based UC systems (Fig. 4b and Fig. S11, see ESI† for details of Φ_{UC}' determination).[25] In general, the quantum yield is defined as the ratio of absorbed photons to emitted photons, and thus the maximum yield (Φ_{UC}) of the bimolecular TTA-UC process is 50%. However, many reports multiply this value by 2 to set the maximum efficiency at 100%. To avoid the confusion between these different definitions, the UC efficiency is written as Φ_{UC}' (= $2\Phi_{\mathrm{UC}}$) when the maximum value is normalized to 100%. Interestingly, the Φ_{UC}' value remained unchanged by diluting Al-**An**-**Por** solution from 4 mM to 0.04 mM (Fig. 4b). This result supports that TTET and TTA processes mainly occur within the coordination copolymers. This dilution-tolerant UC efficiency was achieved by the strong Al-O coordination bonds,[33] and the stability of photon-upconverting nanofibers promises potential applications in wide disciplines.

In conclusion, we demonstrate the concept of design translation from solid-state MOF chemistry to the solution-based, dimension-controlled supramolecular chemistry. The novel photofunctional supramolecular nanofibers are constructed by the complexation between Al^{3+} ions and alkyl chain-modified chromophoric ligands. The lipophilic design approach for coordination copolymers allows the homogeneous integration of multiple chromophores with totally different size and shape assemblies at desired compositions. Moreover, the coordination copolymers show the appropriate molecular arrangements of chromophores that effectively avoid concentration quenching and achieve efficient triplet energy migration, resulting in efficient TTA-UC emission even at the low concentration condition. The generalization of the current concept in other wavelength regions such as near infrared (NIR)-to-visible TTA-UC is currently under investigation in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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