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All-or-none switching of photon upconversion in self-assembled organogel systems†

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Aggregation-induced photon upconversion (iPUC) based on a triplet–triplet annihilation (TTA) process is successfully developed *via* controlled self-assembly of donor–acceptor pairs in organogel nanoassemblies. Although segregation of donor from acceptor assemblies has been an outstanding problem in TTA-based UC and iPUC, we resolved this issue by modifying both the triplet donor and aggregation induced emission (AIE)-type acceptor with glutamate-based self-assembling moieties. These donors and acceptors co-assemble to form organogels without segregation. Interestingly, these donor–acceptor binary gels show upconversion at room temperature but the upconversion phenomena were lost upon dissolution of the gels on heating. The observed changes in TTA-UC emission were thermally reversible, reflecting the controlled assembly/disassembly of the binary molecular systems. The observed on/off ratio of UC emission was much higher than that of the aggregation-induced fluorescence of the acceptor, which highlights the important role of iPUC, *i.e.*, multi-exciton TTA for photoluminescence switching. This work bridges iPUC and supramolecular chemistry and provides a new strategy for designing stimuli-responsive upconversion systems.

1 Introduction

Photon upconversion through annihilation between two long-lived excited triplets, namely triplet–triplet annihilation-based photon upconversion (TTA-UC),

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has recently generated a great deal of interest because of its wide applications ranging from renewable energy technologies to bioimaging and phototherapy.[1–10] The major advantage of TTA-UC compared with the other UC mechanisms is its occurrence with low-intensity and non-coherent incident light. Generally, TTA-UC requires a pair of donors (D, sensitizer) and acceptors (A, emitter) (Fig. S1†) which are molecularly dissolved in deaerated solution. This UC mechanism starts with the photoexcitation of the donors to the singlet state, which then undergoes intersystem crossing (ISC) to the triplet state. The encounter of these triplets with ground-state acceptors causes triplet–triplet energy transfer (TTET), giving optically dark, metastable acceptor triplets. The subsequent diffusion and collision of two excited acceptor triplets generate a higher energy singlet state, from which unconverted fluorescence is emitted. Because of the long lifetime of triplet species, the intensity of the excitation light can be reduced to the order of a few mW cm^{-2} which is comparable to the solar irradiance at a specific excitation wavelength. The TTET and TTA processes occur *via* an electron exchange mechanism (Dexter energy transfer),[11] which shows an exponential dependence on the intermolecular distance. Thus, to facilitate these processes, molecules need to be in close proximity to allow the overlap of wave functions or at least within the distance of *ca.* 1 nm. Furthermore, fast diffusion of excited triplet molecules holds a key to achieving efficient TTA-UC under very weak incident light, where conventional molecular diffusion-based TTA-UC in solutions or polymer matrices have distinct limitations.[8,9]

Molecular self-assembly provides a powerful solution to overcome these issues.[9,12–17] The ordered molecular systems of D and A show controllable and efficient TTA-UC by virtue of efficient TTET and triplet energy migration (TEM) among regularly aligned acceptor chromophores.[9,13–17] This TEM-UC not only allows efficient UC quantum yields at solar irradiance, but also a handle on switching the UC emission, known as aggregation-induced photon upconversion (iPUC).[18] While most examples of aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) are based on singlet excited states and single-exciton phenomena,[19–22] iPUC is a multi-exciton process using triplet excited states, which enables an extremely high on/off ratio.[18] When a triplet state of a cyano-substituted distyrylbenzene, (2*Z*,2′*Z*)-2,2′-(1,4-phenylene)bis(3-phenylacrylonitrile) (DCS),[19] was sensitized in solution, no UC emission was observed. In stark contrast, crystalline DCS revealed clear upconverted emission. However, in this solid acceptor system, serious segregation of donor molecules from the host occurred as reported for binary crystalline D–A pairs,[6] which is not desirable for efficient donor-to-acceptor TTET. It is anticipated that the extension of iPUC to molecular self-assemblies in solution would not only resolve this issue but also provide an opportunity to develop signal-responsive TTA-UC systems.

Here we report a new supramolecular iPUC system that shows reversible on/off switching of UC emission depending on the temperature. Inspired by the excellent gelatinizing behavior of glutamate derivatives,[12,14,23–25] we modified DCS (acceptor) and Pd(ii) mesoporphyrin IX (donor) with lipophilic L-/D-glutamate units containing multiple amide groups (Fig. 1). The obtained new acceptors (**L-1**/**D-1**) show gelation-induced enhanced fluorescence which reflect the AIE nature inherent to the DCS unit. The obtained new donor (**L-2**) is miscible with acceptors **L-1**/**D-1** to form binary D–A gels in a variety of solvents, giving clear TTA-UC emission. In contrast, on elevating the temperature, these D–A gels dissolved and was accompanied by the loss of upconverted emission. Thus, introducing the molecular design of hydrogen bond-promoted organogelators allowed the homogeneous mixing of D–A pairs in molecular assemblies with thermally controlled iPUC characteristics.

2 Materials and methods

2.1 Materials

All reagents and solvents were used as received unless otherwise indicated. The synthesis details of **L-1**, **D-1** and **L-2** are described in the ESI.† Pd(II) mesoporphyrin IX was purchased from Frontier Scientific, Inc. Analytical grade dimethylformamide (DMF), ethanol and toluene were purchased from Wako Pure Chemical. The gel formation was confirmed using inverse tube tests and rheology measurements. The obtained binary D–A gels were strong enough to keep their shape for more than two months without any collapse. To prepare the deaerated gels, first, all the solids and solvent were added to a cell, where some solids remained undissolved. Second, all the gas in the dispersions was removed *via* repeated freeze–pump–thaw cycles. Third, the degassed dispersions were heated

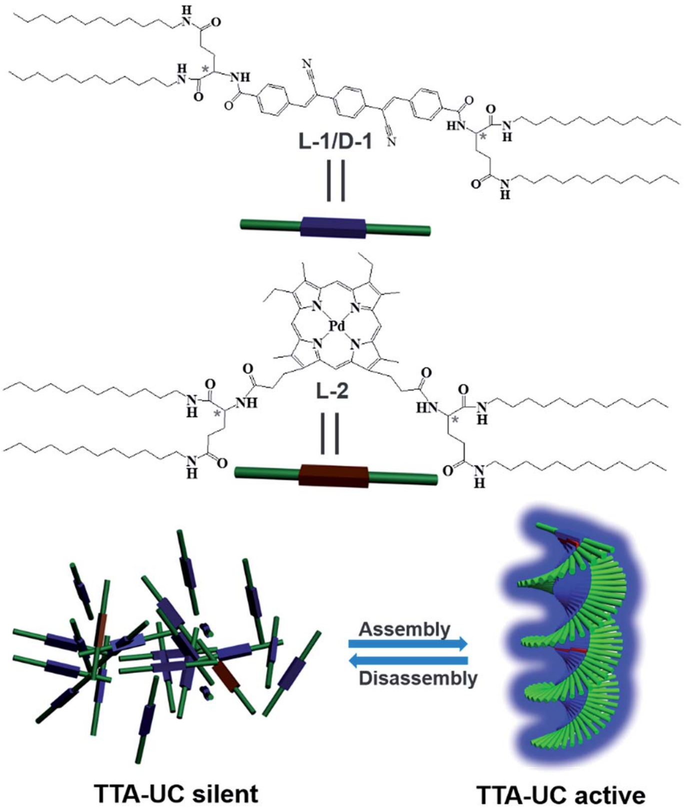

Fig. 1 Schematic illustration of the self-assembly-induced TTA-UC. Acceptor molecules (**L-1** or **D-1**) spontaneously co-assemble with donor molecules (**L-2**) to enable thermal switching of TTA-UC.

for 2–3 minutes at high temperature using a hot water bath until a clear solution was formed, and then the hot solutions were cooled down to room temperature, providing deaerated gels.

2.2 Measurements

UV-vis absorption and luminescence spectra were recorded on a JASCO V-670 spectrophotometer and a PerkinElmer LS 55 fluorescence spectrometer, respectively. CD and CPL spectra were recorded using a JASCO 810 spectropolarimeter and a homemade CPL spectroscopy system.[26] Time-resolved fluorescence lifetime measurements were carried out using a time-correlated single photon counting lifetime spectroscopy system, Hamamatsu Quantaurus-Tau C11367-02 (for fluorescence lifetime)/C11567-01 (for delayed luminescence lifetime). The quality of the fit was judged using fitting parameters such as χ^2 (<1.2) as well as visual inspection of the residuals. The upconversion luminescence spectra were recorded on an Otsuka Electronics MCPD-7000 instrument as the excitation source using external, adjustable semiconductor lasers. Scanning electron microscopy (SEM) pictures of the xerogels were taken on a Hitachi S-5000 (acceleration voltage, 10 kV). The accelerating voltage was 15 kV and the emission was 10 mA. The xerogels were prepared by drying the gels with a JASCO SCF supercritical CO_2 system.

3 Results and discussions

3.1 Supramolecular assembly of L-1/D-1 and spectral properties

The new acceptors **L-1**/**D-1** were synthesized by introducing superior gelation-promoting units *N*,*N*′-bis(dodecyl)-L/D-amine-glutamic diamide (LGAm/DGAm) to a typical AIE chromophore (2*Z*,2′*Z*)-2,2′-(1,4-phenylene)bis(3-phenylacrylonitrile). **L-1**/**D-1** formed organogels when dispersed in a wide range of polar or non-polar solvents. This versatile gelation behaviour is due to the presence of three amide groups connected to the chiral center, which gives stable hydrogen bond networks with the aid of aligned alkyl chains.

The absorption spectra of the **L-1** gels in three different solvents, DMF, ethanol and toluene, show a peak at 350 nm (Fig. S2a†), which is similar to the spectrum of DCS in solution. On the other hand, the fluorescence of the **L-1** gels exhibited solvatochromic characteristics. As shown in Fig. 2a, with increasing solvent polarity, remarkable red-shift and broadening were observed for the emission spectra. The DCS unit is composed of electron donor (aromatic ring) and acceptor (cyano group) units,[27] and such molecules with intramolecular charge transfer characteristics often show solvatochromic effects. Similar to the AIE behaviour of DCS reported by Park *et al.*,[28,29] **L-1** and **D-1** exhibited an enhancement in fluorescence intensity on gelation.[30–32] We selected **L-1** as an example to investigate the luminescence behavior. At 90 °C, **L-1** in toluene solution gave a broad peak at around 490 nm. Upon cooling this solution to room temperature, the peak showed a blue-shift with an increase in fluorescence intensity (Fig. 2b). Similar gelation-induced enhancements in fluorescence intensity were also observed in DMF and ethanol (Fig. S2b and c†).

The chiral assembly structures of **L-1** and **D-1** were further characterized using circular dichroism (CD), circularly polarized luminescence (CPL) measurements

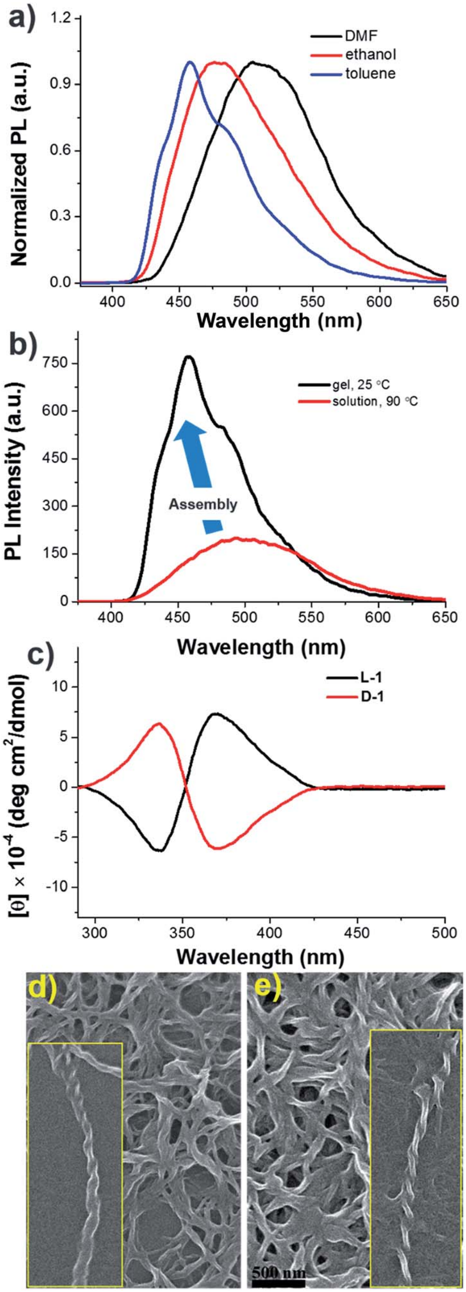

Fig. 2 (a) Normalized fluorescence spectra of **L-1** in various solvents ([**L-1**] = 1 mM, λ_{ex} = 375 nm). (b) Fluorescence spectra of **L-1** in toluene at different temperatures (([**L-1**1] = 1 mM, λ_{ex} = 375 nm). (c) CD spectra of toluene gels made from **L-1** and **D-1** ([**L-1**] = [**D-1**] = 1 mM). SEM images of xerogels of (d) **L-1** and (e) **D-1** made from DMF gels, the inset is the magnified picture of the chiral structures.

and scanning electron microscopy (SEM). The toluene gels of **L-1** and **D-1** show CD spectra with characteristic exciton-coupling, which are in mirror symmetry with respect to the chirality (Fig. 2c). Although **L-1** and **D-1** in DMF and ethanol gels also show mirror-symmetric CD spectra, their CD spectral intensities are weaker than those observed for toluene gels (Fig. S3a and b†). This indicates a higher level of regular chromophore alignment in the toluene gels. The observed CD for these gels clearly shows that the molecular chirality of the glutamate units provided a chiral environment for the aligned DCS chromophores.[33,34] Reflecting the supramolecular chirality, the CPL was observed with an asymmetric factor $g_{\mathrm{lum}} = \pm 4 \times 10^{-2}$ at 470 nm, which is a typical value for organic chiral assemblies.[35] The SEM images of the xerogels prepared by drying the DMF gels showed left-handed (**D-1**) and right-handed (**L-1**) helical fibers with a diameter of about 50 nm (Fig. 2d and e). All these results indicate the chiral self-assembly of **L-1** and **D-1** formed in these solvents.

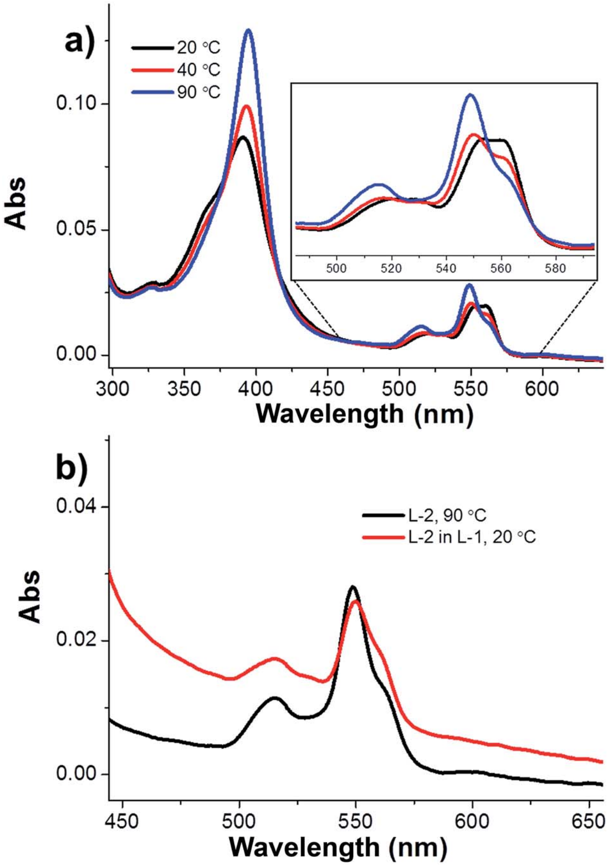

Fig. 3 (a) Temperature dependent UV-vis spectra of **L-2** in toluene ([**L-2**] = 20 μM). Inset, enlarged spectra for the Q-band. (b) Absorption spectra of the **L-2** toluene solution at 90 °C (black line, [**L-2**] = 20 μM) and binary **L-2**/**L-1** gel at 20 °C (red line, [**L-2**] = 20 μM, [**L-1**] = 10 mM).

3.2 Supramolecular co-assembly of the donor and acceptor

As described, the segregation of donors and acceptors was observed for previous solid-state TTA-UC systems.[6,18] We therefore introduced identical self-assembly-directing units with multiple amide bonds in expectation of increasing the cohesive force (hydrogen bonding, solvophobic interactions[36]) that operate between the donor and acceptor molecules. The compatibility of donor **L-2** to acceptor **L-1** in the organogels was investigated using the absorption spectra. The donor **L-2** alone formed a gel in toluene ([**L-2**] = 20 μM) and its Q-band showed temperature-dependent changes which are related to interchromophore interactions (Fig. 3a). A sharp Solet band and Q-band peaks are observed at 394 nm and 549 nm in toluene at 90 °C, which are ascribed to the absorption peaks of monomeric **L-2**. Meanwhile, cooling the solution to room temperature caused

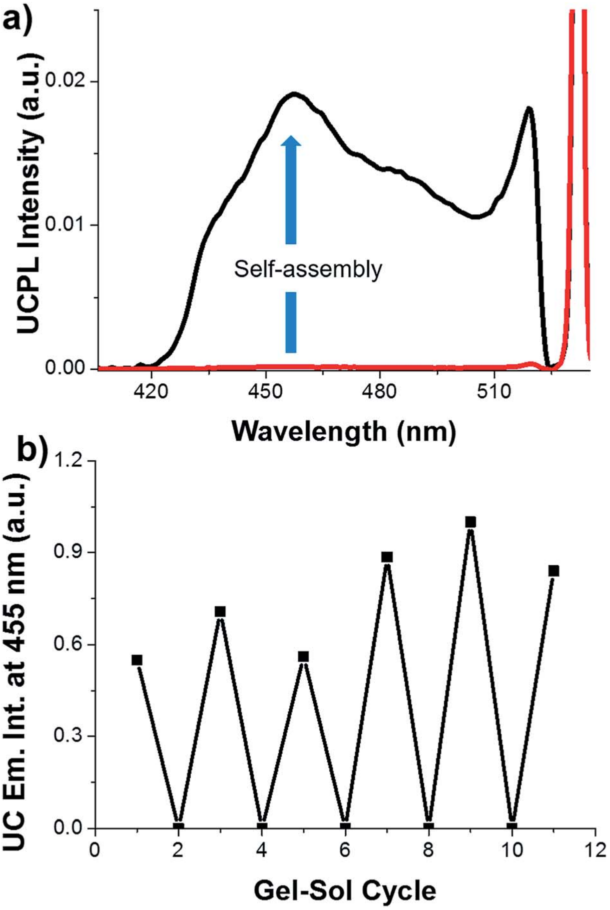

Fig. 4 (a) Photoluminescence spectra of the **L-2**/**L-1** pair in toluene deaerated using repeated freeze–pump–thaw cycles (red line, toluene solution at 90 °C; black line, toluene gel at 25 °C; [**L-2**] = 20 μM, [**L-1**] = 10 mM). Note that the shape of the UC luminescence is influenced by light scattering of the gel and the short pass filter (510 nm) employed. (b) Upconverted emission intensity switching at 455 nm with repeated changes in temperature.

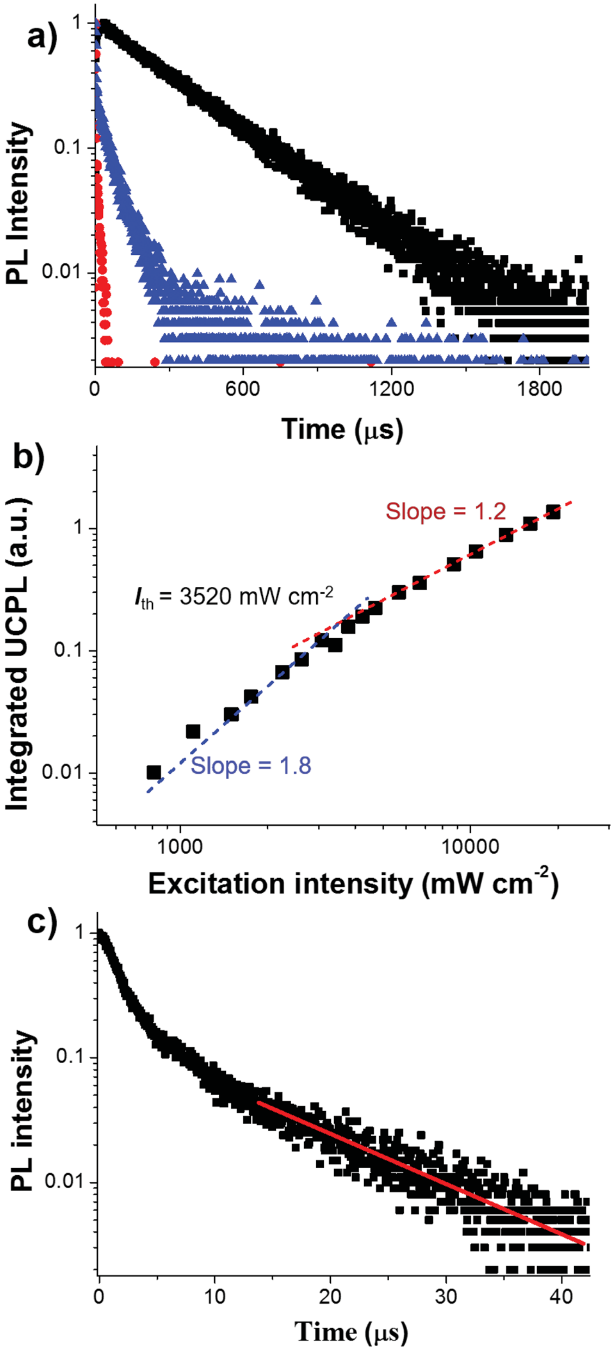

Fig. 5 (a) Decay of the donor **L-2** phosphorescence at 660 nm in the absence (black) and presence (blue) of acceptor **L-1** in deaerated toluene gel ([**L-2**] = 20 μM, [**L-1**] = 10 mM), together with the instrument response function (IRF, red) under a pulsed excitation at 531 nm. (b) UC emission intensity observed for the binary **L-2**/**L-1** gel in deaerated toluene as a function of the excitation intensity of the 532 nm excitation. The dashed lines are fitting results with slopes of 1.8 (blue) and 1.2 (red). The I_{th} was determined to be 3520 mW cm^{-2} from the crossing point of these two lines. UCPL: upconverted photoluminescence.

gelatinization of the solvent which was accompanied by hypochromism in the Solet band and a red-shift of the Q-band to 552 nm with the appearance of a new shoulder component at 560 nm. These spectral changes are consistent with the excitonic chromophore interactions observed in the CD spectra (Fig. 2c).

We then prepared a binary gel of **L-1** (10 mM) and **L-2** in toluene ([**L-2**] = 20 μM). The Q-band absorption peak of **L-2** in the binary gel was almost similar to that of the **L-2** solution observed at 90 °C (Fig. 3b), indicating that **L-2** is molecularly dispersed in the gel-forming self-assembly of **L-1**. The binding of **L-2** to **L-1** at the employed molar ratio did not affect the aggregate morphology of **L-1** or **D-1**, as observed from the SEM of the xerogels (Fig. S4†).

3.3 Supramolecular assembly-regulated TTA-UC

We examined the TTA-UC properties of binary **L-2**/**L-1** gels in various solvents ([**L-2**] = 20 μM, [**L-1**] = 10 mM). Fig. 4a shows the upconverted emission spectra of the binary **L-2**/**L-1** gel in deaerated toluene under excitation with a 532 nm green laser. Scattered incident light was effectively removed using a short pass filter (510 nm). Although no emission was observed in the heated solution regardless of the excitation power (measured up to 19.3 W cm^{-2}), the binary gel showed upconverted emission at 458 nm at room temperature. The shape of the UC emission is naturally similar to the fluorescence of **L-1** directly excited at 375 nm. The observed change in UC emission was reversible with respect to the temperature change, as shown in Fig. 4b.

We previously unveiled the mechanism of such iPUC phenomenon using DCS as the acceptor; the sensitized triplet of DCS in solution immediately decays back to the ground state through conformational twisting around a C=C bond and photoisomerization, whereas this deactivation path is effectively inhibited in the solid state.[18] In the current system, the triplet energy landscapes of the co-assembled **L-1** and **L-2** is similarly controlled based on thermally controlled self-assembly/disassembly processes. Thus, cooperative TTA-UC has been realized based on self-assembly.[13] It is important to note that the observed on/off ratio of UC emission is much higher than that of the aggregation-induced fluorescence of acceptor **L-1** (Fig. 2b), since the iPUC is based on multiple photon phenomena in organized systems and no UC intensity is available in molecularly dissolved solutions due to the rapid deactivation of the excited triplets due to conformational changes.[18]

To further elucidate the TTA-based UC process, the donor phosphorescence lifetime, excitation intensity dependence of UC emission intensity, and UC emission lifetime were studied. Without acceptor, the phosphorescence of **L-2** at 660 nm in the toluene gel showed a single exponential decay with a lifetime of 295 μs (Fig. 5a). Meanwhile, in the presence of acceptor **L-1**, the phosphorescence decay became significantly faster and a lifetime of 64.8 μs was observed. From these results, the donor-to-acceptor TTET efficiency was estimated to be 78%. This good TTET efficiency clearly supports **L-2** being well accommodated by the

(c) UC emission decays at 480 nm of the binary **L-2**/**L-1** gel ([**L-2**] = 20 μM, [**L-1**] = 10 mM) in deaerated toluene under pulsed excitation at 531 nm. The red fitting curve was obtained by considering the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$ (τ_{UC}: UC emission lifetime, $\tau_{A,T}$: acceptor triplet lifetime).[38–40] acceptor **L-1** self-assemblies without segregation, while it would be possible to further improve the TTET efficiency by improving the mutual orientation of the D–A pairs and their triplet energy levels.

In general, the TTA-UC emission intensity shows a quadratic and first-order dependence on the incident light intensity in the low- and high-excitation intensity regimes, respectively. The I_{th} value is experimentally determined as the intersection point of these two lines.[2,37,38] Fig. 5b presents a double logarithm plot for the UC emission intensity of the binary **L-2**/**L-1** gel as a function of incident light power intensity ($\lambda_{\mathrm{ex}} = 532$ nm). A slope closer to 2 was observed in the weak incident light regime, whereas it changed to *ca.* 1 at an excitation intensity above an I_{th} of 3250 mW cm^{-2}. The TTA-based UC mechanism in this binary gel system was further confirmed from the μs-scale decay of the UC emission (Fig. 5c). An acceptor triplet lifetime $\tau_{\mathrm{A,T}}$ of 20 μs was obtained by considering the well-known relationship of $I_{\mathrm{UC}}(t) \propto \exp(-t/\tau_{\mathrm{UC}}) = \exp(-2t/\tau_{\mathrm{A,T}})$ (τ_{UC}: UC emission lifetime, $\tau_{\mathrm{A,T}}$: acceptor triplet lifetime) in the longer timescale region,[38–40] when the annihilation efficiency becomes negligible compared with the spontaneous decay of the triplets. The observed lifetime is relatively short for the metastable acceptor triplet, which may exert a causal influence on the observed relatively high I_{th} value.

The TTA-UC was also confirmed for the gels formed in other solvents (Fig. S5–S7†). The upconversion luminescence in these systems are compared in Fig. S7.† Interestingly, the UC emission intensity value depending on the solvent employed, with intrinsic solvatochromic properties retained in these systems. The I_{th} values in DMF (113 mW cm^{-2}) and ethanol (1110 mW cm^{-2}) were found to be lower than that in toluene (Fig. S6†). This would be due to the longer triplet lifetimes τ_{UC} in ethanol (28 μs) and DMF (35 μs), and apparently fast triplet diffusion also occurred in these molecular assemblies. It is interesting that a simple relationship between the amplitude of the CD signals in these molecular assemblies (Fig. 2c, S3a and b†) and I_{th} values was not observed, although both parameters would potentially be related to the orientational regularity of the DCS chromophores and triplet diffusivity, respectively. This indicates that there are multiple parameters which affect the TTA-UC properties as a whole in these soft molecular systems, which makes the soft molecular assemblies intriguing and provides opportunities to derive unique signal-responsive functions.

4 Conclusions

In this study, we combined the concepts of molecular self-assembly and iPUC. Both donor and acceptor are modified with identical self-assembling moieties, which successfully allowed the molecular distribution of the donor in the self-assembled acceptor gel fibres. They exhibit thermally controlled, reversible on-off switching of UC emission by virtue of controlled assembly/disassembly processes. The current work offers an important bridge between photon upconversion and supramolecular chemistry. The implementation of vast knowledge accumulated in supramolecular chemistry may lead to the development of smart photon upconversion systems responsive to a variety of physical and chemical stimuli.

Acknowledgements

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