

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Dual upconverted and downconverted circularly polarized luminescence in donor-acceptor assemblies

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201804402 Angew. Chem. 10.1002/ange.201804402

Link to VoR: http://dx.doi.org/10.1002/anie.201804402 http://dx.doi.org/10.1002/ange.201804402

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Dual upconverted and downconverted circularly polarized luminescence in donor-acceptor assemblies

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Abstract: Chirality and energy transfer represent two important aspects of structure and function in biological system. Here, through the mimic of both the chiral and energy transfer in an artificial selfassembled system, we not only realized the chiral transfer but also created a dual upconverted and downconverted energy transfer system that emit circularly polarized luminescence. It is found the individual chiral π-gelator can self-assemble into nanofiber exhibiting supramolecular chirality and circularly polarized luminescence (CPL). In the presence of an achiral sensitizer Pd(II) octaethylporphyrin derivative, both chirality transfer from chiral gelator to achiral sensitizer and triplet-triplet energy transfer from excited sensitizer to chiral gelator could be realized. Specifically, upconverted CPL could be observed through a triplet-triplet annihilation photon upconversion (TTA-UC) process, while downconverted CPL could be obtained from chirality-transfer-induced emission of the achiral sensitizer. The interplay between chiral energy acceptor and achiral sensitizer promoted the communication of chiral and excited energy information.

Chirality and energy transfer represent two important aspects of structure and function in biological system. Chiral molecules such as L-amino acids and D-sugars formed the covalent polymers and then self-assembled into helical proteins and DNA through non-covalent bond.^[1] During such process, molecular chirality was transferred to the supramolecular system, which is crucial for the well-implementation of their sophisticated functions like catalytic and replication activity in life process. In addition, the transfer of information in living organisms is multichannel, not only through the chirality-based structural information but also through the electron-, ion-, photon-based energy types.^[2] Many researches have tried to mimic the process through self-assembly strategy.^[3] Unfortunately, most of the researches only focused one aspect, either chirality or energy transfer. Only a limited efforts have been devoted to construction of the supramolecular systems containing both chirality and energy transfer.^[4-5] In these two chirality-related energy transfer systems, high-energy excitation resulted in lowenergy circularly polarized luminescence (CPL). Here, we combined both the chirality and energy transfer in the

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supramolecular assemblies and revealed a new insight into the interplay between the two processes. That is, a dual upconverted and downconverted CPL can be realized simultaneously.

Photon upconversion, the population of higher-energy excited state with excitation at lower-energy light, provides a novel view for achieving higher-energy emission. In this work, we conceived an idea to integrate chiral assembly with photon upconversion (UC) based on triplet-triplet annihilation (TTA) mechanism,^[6] and design a self-assembly system based on anthracene derived chiral gelator (LGAn or DGAn) and achiral Pd(II) octaethylporphyrin derivative (PdOEP-C18) as sensitizer (Figure 1). Here, the achiral PdOEP-18 experiences the chiral environment of LGAn or DGAn after incorporation into the LGAn/DGAn fibers, which generates supramolecular chirality of PdOEP-18 due to the spatial nonsymmetric arrangement of PdOEP-18 in the co-assembly. In term of energy transfer, LGAn or DGAn works as energy acceptor and PdOEP-18 as energy donor in the TTA-based upconversion process. It is found that when chiral LGAn or DGAn assembled with the achiral PdOEP-C18, the chirality transfer from LGAn or DGAn to PdOEP-C18 and triplet-triplet energy transfer from PdOEP-C18 to LGAn (DGAn) can happen simultaneously. The co-assembly exhibited dual upconverted (460 nm) and downconverted CPL (550-750 nm) emission under excitation of a 532 nm laser. With such design, we have successfully integrated with two channels of chirality and energy transfer process and revealed the interplay of energy and chirality transfer to produce a dual CPL simultaneously.



Figure 1. (a) Chemical structures of the chiral gelator LGAn (DGAn) and achiral sensitizer PdOEP-C18 and schematic representation of chirality transfer from chiral gelator to achiral PdOEP-C18 during the coassembly process. (b) Dual upconverted and downconverted CPL emission for donor acceptor coassembly in deaerated condition under excitation of 532 nm laser. The upconverted CPL at 460 nm results from the successful triplet-triplet energy transfer from energy donor (PdOEP-C18) to energy acceptor (LGAn or DGAn assembly), while the downconverted CPL in the range of 550-750 nm results from the successful chirality transfer from LGAn or DGAn to PdOEP-C18.

The designed chiral gelator LGAn or DGAn was shown in Figure 1a, which contains an anthracene unit conjugating with a gelator moiety N,N'-bis(dodecyl)-L(D)-amine-glutamic diamide.^[7] The detailed synthetic route was shown in Figure S1. The

individual self-assembly and properties were first investigated. LGAn or DGAn showed excellent gel ability in various organic solvents. Among them, the gel formed in toluene was transparent. In order to minimize the interference of light scattering in the later research, all the studies were focused on the self-assembly in toluene. The self-assembly behavior of LGAn in solution and gel were studied by absorbance and emission spectra. As shown in Figure S2, the absorbance spectra in solution exhibited three well-resolved absorption peaks at 347, 364 and 384 nm, which can be attributed to the S₀-S₁ transition with different vibronic peaks.^[8] The emission spectrum in solution exhibited well-defined peaks at 412 and 426 nm. When increasing the concentration to 2.5 mM, transparent gel formed. The absorption of the gel broadened and still exhibited some well-resolved vibronic peaks. The emission spectrum had a bathochromic shift to 445 nm with the disappearance of vibronic peaks, which indicated the formation of ordered self-assemblies in the gel. When the concentration was further increased to 5 to 20 mM, the vibronic peaks tended to disappear and the emission spectra shifted to 455 nm, indicating a dense molecular packing. We further measured the variable temperature photoluminescence spectrum to confirm the self-assembly. As shown in Figure S3, the emission peak gradually hypsochromic shifted upon heat-driven disassembly and moved to 428 nm at 60 °C. It should be noted that the emission intensity of the system decreased with the increase of temperature, which was suggestive of the aggregation induced fluorescence enhancement for LGAn system.^[9] The selfassembled structures of the gel were further investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). As shown in Figure S4-5, thin and entangled fibers were formed.

Since the gelators have chiral centers, the gel were characterized by CD spectra, as shown in Figure 2a. LGAn gel showed positive Cotton effect at 375 nm, which is corresponding to the absorption region of anthracene chromophore, indicating that molecular chirality could be amplified through the supramolecular self-assembly.^[10] The DGAn gel showed mirror-imaged CD signal with LGAn, suggested that the supramolecular chirality followed the molecular chirality. The temperature-dependent CD spectra (Figure S6) further confirmed such chirality transfer.



Figure 2. (a) CD (up) and UV-vis spectra (down) of LGAn and DGAn gel. (b) CPL spectra of LGAn and DGAn gel. For the measurement of CD and CPL, the [LGAn] = [DGAn] = 10 mM. $\lambda ex = 350 \text{ nm}.$

The gel was further found to show circularly polarized luminescence (CPL), which is used to evaluate the chirality of excited-state.^[11] As shown in Figure 2b, CPL signals with different handedness and emission at 460 nm could be observed. It further revealed that LGAn gel with a positive

Cotton effect displayed a left-handed CPL, while the DGAn a right-handed CPL. The magnitude of CPL was evaluated by the luminescence dissymmetry factor (g_{lum}),^[12] which were about 1.3 \times 10⁻³ and -1.1 \times 10⁻³ for LGAn or DGAn gel, respectively, comparable to many organic self-assembly system.^[13] Sergio Abbate and co-authors have stressed that the measured CPL should be corrected when fluorescence (and CPL) of the targeted sample is too close in wavelength to absorption (and CD).^[14] In our present study, the absorption (and CD) of our gel sample has only a slight overlap with the fluorescence (and CPL). Therefore, the correction equations shown in the two references were not applied for our present case due to different setup.



Figure 3. (a) Normalized absorption (solid line) and luminescence (dotted line) spectra for PdOEP-C18 solution (2.8×10⁻⁵ M, red line, $\lambda_{ex} = 532$ nm) in deaerated toluene and LGAn gel (10 mM, blue lines, $\lambda_{ex} = 350$ nm). (b) Upconversion emission spectra of LGAn/PdOEP-C18 = 100/1 (mol/mol) gel in deaerated toluene excited with different incident power intensity of 532 nm laser at room temperature. A notch filter at 532 nm was used to remove the scattered incident light in front of the detector. (c) Dependence of UC intensity at 460 nm on the excitation density. The solid lines are fitting results with slope of 1.7 (blue) and 1.2 (red) in the low- and high-power density regimes, respectively. (d) Time resolved upconverted emission at 460 nm of the EGAn/PdOEP-C18=100/1 gel in deaerated toluene under 532 nm laser excitation at room temperature. The tail fit (red circle), [LGAn] = 10 mM. The excitation density of 532 nm laser was 930 mW cm⁻².

We then investigated the co-assembly behavior and energy transfer in the cogel of LGAn (DGAn) with PdOEP-C18. PdOEP is a typical energy donor for sensitizing the triplet of acceptor in TTA-UC process.^[6e, 6i, 6j, 15] Here, for improving the coassembly ability of sensitizer with the energy acceptor LGAn (DGAn), two long alkyl chains were introduced. As a typical sensitizer for TTA-UC, PdOEP-C18 in deaerated toluene exhibited a typical Soret band at 391 nm and Q bands at 525 nm and 556 nm in the absorption spectrum, and one phosphorescence peak at 670 nm (Figure 3a).^[6e, 6i, 15] Figure 3b shows upconverted emission of LGAn gel doped with PdOEP-C18 excited under various incident 532 nm laser power. Blue UC emission were observed upon excitation of the cogel system by 532 nm green laser. The location of the UC emission (λ_{ex} = 532 nm) is similar to that of the normal fluorescence (λ_{ex} = 350 nm). The phosphorescence of sensitizer PdOEP-C18 was severely quenched regardless of the excitation power, indicating the efficient TTET from sensitizer to the acceptor LGAn.^[6b, 16f] This can be further confirmed by the reduced phosphorescence lifetime of PdOEP-C18 in the

presence of LGAn compared with that in the absence of LGAn (Figure S7). To gain insight into the TTA-based UC mechanism, the dependence of UC emission intensity to the excitation power density was investigated. Figure 3c presents a double logarithm plot for the UC emission intensity of PdOEP-C18-doped gel as a function of incident light power density (λ_{ex} = 532 nm). The blue line and red line are the fitting results with slopes of 1.7 and 1.2 in the low and high excitation power density regime, respectively. It provides decisive experimental evidence for TTA-based photon UC in the hybrid gel system.^[6b, 16] A high crossover threshold 4350 mW cm⁻² was obtained, above which TTA becomes the main triplet deactivation channel for the acceptor. A long UC emission lifetimes at 460 nm for LGAn/PdOEP-C18 (τ_{UC} = 135 µs, Figure 3d) and DGAn/PdOEP-C18 (τ_{UC} = 126 µs, Figure S8) were observed, which is significantly longer than the pure acceptor LGAn (18.5 ns; λ_{ex} = 350 nm; Figure S9). Such prolonged luminescence decay is characteristic of the TTA-UC processes.^[6b, 17] Thus, a light-harvesting supramolecular system with high UC efficiency was successfully fabricated based on donor-acceptor (D-A) self-assembled system.



Figure 4. (a) CD (up) and absorption (down) spectra for gels of LGAn/PdOEP-C18 = 20/1 (molar ratio) and DGAn/PdOEP-C18 = 20/1 (molar ratio); (b) Temperature-dependent UV-vis absorption spectra of LGAn/PdOEP-C18=20/1 co-gel. The measurement was conducted in 1mm sealed quart cell. The absorption of LGAn in this condition was too large, so the spectra just shown the absorption region of PdOEP-C18. (c) CPL spectra of LGAn/PdOEP-C18 = 100/1 (molar ratio) and DGAn/PdOEP-C18 = 100/1 (molar ratio) in deaerated toluene excited by 532 nm laser with excitation density at 7847 mW/cm²; 532 nm notch filter was placed between the sample and detector perpendicular to the optical path; (d) CPL spectra of LGAn/PdOEP-C18 = 100/1 (molar ratio) and DGAn/PdOEP-C18 = 100/1 (molar ratio) in deaerated toluene excited by 532 nm laser with excitation density at 7847 mW/cm²; 532 nm laser with excitation density at 7847 mW/cm² is spectra of LGAn/PdOEP-C18 = 100/1 (molar ratio) and DGAn/PdOEP-C18 = 100/1 (molar ratio) in deaerated toluene excited by 532 nm laser with excitation density at 23439 mW/cm²; 532 nm long pass filter was used. [LGAn] = [DGAn] = 10 mM. During the measurement of CPL, a low slit width value at 500 µm in detector was used to reduce the stray light, thus a hole in emission at 532 nm could be clearly observed.

Since LGAn (DGAn) as energy acceptor exhibited supramolecular chirality in the self-assembly, we further studied the interplay between the chirality and energy transfer. We first measured the CD spectra of LGAn/PdOEP-C18 at 100/1 molar ratio. As shown in Figure S10, the absorption and CD signal of PdOEP-C18 in this low concentration is weak but observable, which indicated that the successful chirality transfer from LGAn to PdOEP-C18 occurred in LGAn/PdOEP-C18 co-gel. In order to clarify the chirality transfer in co-gel more clearly, we conducted the CD measurement at 20/1 ratio. The CD spectrum of the coassembly of LGAn/PdOEP-C18 showed two negative CD bands in the range of 500-600 nm, while DGAn/ PdOEP-C18 showed two positive ones in the same range (Figure 4a). In LGAn/PdOEP-C18 assembly, two exciton type Cotton effects were observed, which is strongly suggestive that PdOEP-C18 could capture the supramolecular chirality from the chiral assemblies. Temperature-dependent absorption spectra further confirmed this (Figure 4b). The absorption peaks located at 560 nm and 523 nm in gel at 25 °C gradually hypsochromic-shifted to 549 nm and 514 nm when the temperature was increased to 80 °C, indicating a certain J-aggregation for PdOEP-C18 in the cogel.^[4, 18] FTIR was further used to gain insight into the driving force for the gel formation. As shown in Figure S11, strong vibrations were observed at 3296, 1636 and 1554 cm⁻¹, which can be ascribed to N-H stretching vibration, amide I and II band hydrogen bonding state, respectively.^[4, 19] As for in LGAn/PdOEP-C18, the amide I band and II band were identical to that of pure LGAn, which further confirmed that the addition of PdOEP-C18 did not destroy the well-ordered packing of LGAn.

The co-assembly showed upconverted circularly polarized luminescence (UC-CPL). As shown in Figure 4c, LGAn/PdOEP-C18 cogel in deaerated toluene exhibited positive UC-CPL signal at 460 nm under 532 nm laser excitation with excitation density at 7847 mW/cm², while DGAn/PdOEP-C18 cogel exhibited the mirror-imaged signal. The signs of UC-CPL at 460 nm were the same as that excited with 350 nm (Figure 2b). To date, the only study on upconverted circularly polarized luminescence was reported in our recent published work.^[6d] we realize the upconverted circularly polarized Here. luminescence in supramolecular self-assembly system again. More interestingly, the energy donor PdOEP-C18 exhibited a weak phosphorescence emission at 670 nm due to high TTET efficiency in the LGAn/PdOEP-C18 cogel system, as shown in Figure 4c. If we increase the excitation laser power, to say, 23 W/cm², then we can see the CPL more clearly. As shown in Figure 4d, the cogel system exhibited obvious emission intensity in the wide range of 550-750 nm and strong CPL signal. This strongly suggested that PdOEP-C18 can emit downconverted CPL in the assembly at deaerated condition. Thus, a dual CPL emission including upconverted CPL at 460 nm and downconverted CPL in the range of 550-750 nm was succefully realized in donor-acceptor co-assembly.



Figure 5. The symbol "D" and "A" represent the energy do-nor PdOEP-C18 and energy acceptor LGAn or DGAn in TTA-UC process. (a) In the

coassembly system, the chirality can be transferred from LGAn or DGAn to PdOEP-C18 through entanglement of hydrophobic chains. (b) In the adsorption assembly system, chirality transfer was blocked due to weak interaction between LGAn (DGAn) and PdOEP-C18.

It should be further noted that the assembly pathway has a significant impact on the final assembly structure as well as the properties. We compared the co-assembly of donor and acceptor via co-gelation with the system of simply adsorption (Figure 5). In the adsorption assembly pathway, LGAn (DGAn) gelator was first assembled into supramolecular gel, and then PdOEP-C18 solution was allowed to freely diffuse into the gel matrix. In this case, the chirality transfer from LGAn (DGAn) gelator to PdOEP-C18 could not be realized (Figure 5b). In addition, LGAn/PdOEP-C18 or DGAn/PdOEP-C18 in deaerated toluene formed by adsorption pathway showed only upconverted CPL at 460 nm excited with 532 nm, while without downconverted CPL (see the experimental details in Figure S12). Although larger excitation power at 23439 mW/cm² was used, no downconverted CPL can be observed (Figure S13). This result indicated that the ordered arrangement of the donor and acceptor are vitally important in realizing the dual upconverted and downconverted CPL.

In summary, inspired by the sophisticated information propagating in biological systems, we developed a supramolecular system which exhibit transmission and communication of both chiroptical information and excited energy. Coassembled UC arrays, which were composed of achiral energy donor and chiral energy acceptor, showed dual upconverted and downconverted CPL under the 532 nm laser excitation. The integration of TTA-UC with chirality transfer in assembled system thus renovates the field by introducing the chiral assembly regulated triplet energy transfer. The concept of molecular self-assembly regulated interplay between chiral information and excited energy provides a new perspective for designing chiral functional materials.

Acknowledgements

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB12020200), National Natural Science Foundation of China (51673050 and 91027042); The Ministry of Science and Technology of China (2016YFA0203400) and New Hundred-Talent Program research fund of the Chinese Academy of Sciences. Key Research Program of Frontier Sciences, CAS, (QYZDJ-SSW-SLH044).

Keywords: supramolecular chirality • self-assembly • circularly polarized luminescence • upconversion

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Layout 1:

COMMUNICATION

Dual upconverted and downconverted circularly polarized luminescence could be realized in a composite self-assembly system, which integrated with chirality and triplet-triplet energy transfer process.



Dong Yang, Pengfei Duan*, Minghua Liu*

Page No. – Page No. Dual upconverted and downconverted circularly polarized luminescence in donor-acceptor assemblies