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Universal Reservior of UV, WL and NIR Light for Long Persistent Luminescence from a Metal-Organic Supramolecular Box

Zheng Wang, Cheng-Yi Zhu, Shao-Yun Yin, Zhang-Wen Wei, Jian-Hua Zhang, Ya-Nan Fan, Ji-Jun Jiang, Mei Pan,* and Cheng-Yong Su

Abstract: Long persistent luminescence (LPL) materials have unique photophysical mechanism to store light radiation energy for subsequent release. However, in comparison to the common UV source, white-light (WL) and near-infrared (NIR) excited LPL is scarce. Here we report a metal-organic supramolecular box based on a D- π -A type ligand. Due to the integrated one-photon absorption (OPA) and two-photon absorption (TPA) attributes of the ligand, heavy atom effect of the metal-center, as well as π -stacking and J-aggregation states in the supramolecular assembly, LPL can be triggered by all wavebands from UV, WL to NIR region for the first time. This novel designed supramolecular kit to afford LPL via both OPA and TPA pathways provides potential applications in anti-counterfeiting, camouflaging, decorating, displaying, and so on.

Long persistent luminescence (LPL), also known as afterglow luminescence, is a fascinating optical phenomenon which has certain amount time of emission after removing the excitation light source.^[1] In the past decades, a number of LPL materials have been designed and synthesized by different methods, and attracted considerable attention in various fields including LEDs, displays and decorations, sensors, anticounterfeiting barcodes, military night-visions, bio-imaging lables and so on.^[2-4] However, most of the applicable LPL systems are inorganics doped by rare earth or noble transition metals,[5-7] which have limitations in structural and functional modification and large-scale production due to expensive cost and harsh synthetic conditions. Recently, organic-based LPL materials have been gradually developed by several strategies, including the construction of pure organic solids or host-quest co-crystals, metal-organic hybrids and metal-organic frameworks, etc. [8-13] However, the LPL in so far explored materials is dominantly triggered by one-photon absorption (OPA) of UV light, although some recent studies have expanded the radiation to visible white-light.^[3,5] In comparison, LPL excited by near-infrared (NIR) source remains basically in blank, which might have the merits of low energy and deep penetrability, and can be more applicable in such fields as biological imaging and military anticounterfeiting.[14]

Alternatively, two-photon excited fluorescence (TPEF) provides the utilization of low energy visible/NIR excitation *via* a two-photon absorption (TPA) pathway to produce higher-energy emissions, which is of practical importance for a wide range of applications in optoelectronics and biological fields.^[15] For this

purpose, numerous materials with TPEF potentials have been developed. One of the designing concepts is to construct D- π -A type molecules for the generation of excellent two-photon absorption ability.^[16-18] Bearing above considerations in mind, we herein designed a unique D- π -A type organic ligand from terpyridine derivatives, endowed with both good OPA and TPA attributes. Further coordination with heavy metal Cd(II) ions leads to M₂L₂ rectangular box. As a whole, the inter- and intramolecular packing states among the boxes facilitate triplet excitons and lead to unprecedented LPL with wide excitation of UV, WL and NIR source *via* OPA or TPA pathways.

The D-π-A type organic ligand HTzDPTpy (L) was synthesized by three steps (Figure 1 and Scheme S1), which consists of a conjugated terpyridine, a biphenyl and a tetrazolyl group, acting as the electron-acceptor, π-bridge and electrondonor, respectively. Hydrothermal reaction of HTzDPTpy with CdCl₂ in DMF and H₂O for 2 days at 140 °C afforded yellow block crystals, which were determined to have the formula of $[Cd_2(TzDPTpy)_2(HCOO)_2]\cdot 3H_2O$ (named as Cd_2L_2 , MOC-38). Single crystal X-ray diffraction analysis reveals that Cd₂L₂ is crystallized in monoclinic crystal system belonging to C2/c space group (Tables S1, S2). The phase purity is verified by PXRD, and TGA shows good thermal stability up to ~300 °C (Figures S1, S2). In the crystal structure of Cd₂L₂, two Cd(II) metal centers link two TzDPTpy⁻ ligands to form a rectangular molecular box. Due to the simple yet unique structure of the molecular box consisting of near-parallel sides with polyaromatics, strong π - π stacking interactions are formed. Further intramolecular π - π , C-H... π and C-H...N interactions along different directions stack Cd₂L₂ boxes into a closely-packed 3D framework, leading to *J*-aggregation conformations (Figures S3, S4). This kind of intramolecular packing might promote the population of lower-energy triplet states, as confirmed by the redshift of solid state absorption in comparison with the solution state (Figure S5). This is different from the H-aggregation observed in pure organic LPL materials.^[19] Meanwhile, the abundant inter- and intramolecular interactions also bring restricted molecular motions and reduced non-radiation energy consumption. All these will be helpful to enrich and improve the photophysical properties of Cd₂L₂, and encourage us for further exploration.

HTzDPTpy shows rather broad absorption spectra extending from 250 to 700 nm (Figure S5), and emits strong blue luminescence centered at 495 nm in air at RT under the excitation of 280 to 400 nm UV light (Figure S6), which can be assigned to the typical π - π * singlet transitions of the ligand. A short decay lifetime of 4.08 ns detected at the emission peak at 495 nm confirms the attribution of fluorescence (F). After pumped to vacuum, the emission intensity was decreased while a broadened contour appears, showing some hints for the emergence of lower energy triplet transitions, which are basically

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obscure in air at room temperature (Figure S7). Additionally, moderate increase of emission intensity and decay lifetime (τ = 9.7 ns) was detected as the temperature gradually decreases from RT to 77 K. This is because the low temperature can

stabilize the molecular vibration and reduce non-irradiation loss. Expectedly, as a wonderful D- π -A type organic molecule, TPEF was obtained for HTzDPTpy using 780 nm laser radiation, with similar attribute of the OPA luminescence (Figure S8).



 Cd_2L_2 Molecular Box: π - π stacking & heavy metal effect Intramolecular Packing & *J*-Aggregation

Figure 1 Design concepts for the targeted metal-organic molecular box with long persistent luminescence by UV, WL and NIR radiation. The inset shows proposed energy transfer mechanism (F, fluorescence; P, phosphorescence; LPL, long persistent luminescence; WLE, white-light emission; OPA, one-photon absorption; TPA, two-photon absorption; UV, ultraviolet; WL, white-light; NIR, near-infrared; S, singlet; T, triplet; ISC, intersystem crossing)

Intriguingly, for the assembled Cd_2L_2 molecular box, dual emissions can be distinguished obviously in the range of 400 to 700 nm under UV light excitation (Figure 2). The blue luminescence centered at 460 nm has a quick decay lifetime of 3.65 ns (RT), which can be assigned to ligand-centered (LC) fluorescence similar to that observed for HTzDPTpy, with some blue-shift due to the metal coordination. Whereas another orange luminescence extends into long wavelength region, with the center basically located at ~610 nm. This emission manifests a slow decay lifetime of 21.4 ms at 298 K, and can be unambiguously ascribed to room temperature phosphorescence (RTP) originating from the triplet excited states of the ligands. The appearance of RTP in Cd₂L₂ metal-organic coordination box which is obscure in pure HTzDPTpy ligand should be contributed to multiple inter- and intra-molecular π - π *, C-H...N, C-H...π packing interactions and J-aggregation as stated above.^[19] Meanwhile, the heavy metal effect of Cd(II) ions also helps to stabilize the triplet energy states and facilitate RTP.

The above dual-emission attributes of Cd_2L_2 consisting of both blue fluorescence and yellow phosphorescence simultaneously provides possibility for single-component whitelight emission (SC-WLE). Adjustment of the excitation wavelength can further modulate the relative intensities of the dual emissions. As shown in Figures 2a and S9, with the steady increase of excitation wavelength from 280 to 450 nm, the relative intensity of I_P/I_F (I_P and I_F means for the intensity of phosphorescence and fluorescence, respectively) is gradually increased. As a consequence, the overall emitting color of Cd_2L_2 changes from blue to orange (Figures 2b and S10, Table S3, S4). Noticeably, at the excitation of 405 nm, a pure white light emission was obtained with the CIE coordinate of (0.33, 0.34).

To further clarify the dual emissions of Cd_2L_2 , varianttemperature photoluminescence was detected at the excitation of 365 and 405 nm, respectively (Figures S11-13, Table S5). When excited at 365 nm, the emission intensities of both blue fluorescence and orange phosphorescence are gradually decreased with the temperature increasing from 77 to 400 K. Analysis of activation energy from Arrhenius equation gives an activation energy to be 1829 J, corresponding to the difference between energies of the two emission states. Nevertheless, the overall emission color keeps basically unchanged in the blue light region (Figure 2c). While at the excitation of 405 nm, as the temperature increases from 77 to 300 K, the intensity of the blue fluorescence shows an abnormal enhancement, in contrast with the abatement of the orange phosphorescence. As a result, the overall emission color is greatly switched from orange to blue region (Figure 2d). This manifests that the emission property of Cd₂L₂ is not only dependent on the excitation energy, but also responds to the temperature, and the PL color changes can be detected by naked eyes. The good linear relationship between CIE coordinate and temperature due to the dual emissions affords a prototype for ratio-dependent thermometer with selfcalibration ability. Time-dependent decay study reveals an obvious increment of the phosphorescence lifetime at low temperature (109.6 ms at 77 K, Figure S14). Time-gated emission spectra show that, with different delayed times from 0.05 to 15 ms, Cd_2L_2 manifests the emission peak at approximately 610 nm, corrpesonding to the room temperature phosphorescence (RTP, Figure S15), further approving of its triplet nature.

Based on the above one-photon excited emission, when using 780 nm wavelength laser as the incident light, efficient TPEF was detected for Cd_2L_2 sample. As shown in Figure S16, a linear log(I)-log(P) relationship can be established between the TPEF intensity (I) and laser power (P), proving the upconverted luminescence is indeed induced by a nonlinear TPA

process. Notably, the TPEF excitation wavelength of Cd_2L_2 can be extended from 780 to 900 nm (Figures 2e, f), showing good adaptability to the excitation energy range, which has been rarely reported in metal-organic coordination systems.



Figure 1. OPA (a-d), TPA (e, f) and LPL (g, h) emissions of Cd_2L_2 in solid state at room temperature. a) OPA emission spectra, and b) CIE coordinates at different excitation wavelength. c, d) variant-temperature emission at the excitation wavelength of 365 and 405 nm. e, f) 1D and 2D TPA fluorescence spectra. g, h) 1D and 2D LPL spectra after radiation of white light. Color from red to blue indicates decrease in emission intensity within f and h.

More fascinatingly, besides the above OPA and TPA luminescence, Cd₂L₂ can give LPL after the removal of different kinds of irradiation source (Figures 2g, h, 3, S17-23, Videos 1-4). Typically, for a single-crystal of Cd_2L_2 with yellow color, prompt blue luminescence is emitted at the excitation of 365 nm UV light. While after the cease of UV-irradiation, long persistent red luminescence is detected. Such is also the case for bulk powder sample of Cd₂L₂ (Figures 3b, S17). Changing the light source to 405 nm, prompt white light emission is generated due to the dual emissions, as discussed before in Figure 2b. While after turning off the white light, red afterglow luminescence is observed to last several seconds. By the aid of a time-dependent spectrophotometer, we successfully recorded the evolution of LPL spectra centered at about 650 nm for Cd2L2 after the removal of 365 or 405 nm UV light for different irradiation time (Figures S18, 19). It can be concluded that basically, the 405 nm irradiation leads to stronger initial LPL intensity than 365 nm light source on equal basis of other conditions (Figure S20), showing that the lower energy excitation might be more favorable for the LPL generation. But notably, extending the irradiation time of 405 nm results in an obvious decrease of the LPL intensity,

while that for 365 nm changes little, which might be due to the heat dissipation effect is more significant in the former.



Figure 3. a) LPL photos of Cd_2L_2 bulk powders at different time interval after the removal of WL radiation. b) Photos of Cd_2L_2 single crystal (upper) and bulk powder (lower) samples at different irradiation source (from left to right, naked eye-detectable yellow color under daylight (WL), OPA or TPA blue luminescence by 365 or 780 UV/NIR excitation, and red LPL after the removal of UV/NIR radiation. c) LPL photos of Cd_2L_2 bulk powders at different time interval after the removal of NIR radiation (room temperature).

Furthermore, more readily available white light, such as the flashlight from a torch or cellphone was selected as the irradiation source. And the red LPL can be triggered even more efficiently and last for several minutes observable by naked eyes after the WL off. The evolution spectra were also recorded by time-dependent spectrophotometer (Figures 2g, 2h, 3a, S21, and Video 2). For the generation of this strong white-lightexcited LPL, the overlapped region of the excitation spectrum of Cd₂L₂ and the irradiation spectrum of the flashlight (Fig. S22) might account. And the WL-excited LPL of Cd2L2 should still be mainly attributable to OPA pathway, similar with the UVirradiation source. Photo-stability of Cd2L2 has been approved by PXRD and repeatability of its LPL has been tested for eight runs (Figure S23), showing good consistence. Moreover, it is even delighted to find that, TPA process can also lead to LPL in Cd₂L₂. As discussed before, blue TPEF can be generated by 780 nm or longer wavelength laser excitation. And after switching off the laser, red LPL appears, which is recorded and can last for several seconds detectable by naked eyes (Figures 3b, 3c, S24, and Videos 3, 4). As far as we know, this is the first report of LPL to be triggered by widebands covering UV, WL to NIR region via either an OPA or TPA pathway, and represents the first example of TPA-LPL.

TD-DFT calculation was performed to explore the mechanism of the fluorescence and phosphorescence emissions of Cd_2L_2 . We can see that, the HOMO and LUMO orbitals of Cd_2L_2 are mainly resided on the biphenyl-tetrazole and terpyridine groups, respectively, in accordance with the D- π -A nature of the ligand. And as shown in Figure 4a and Table S6, there exist multiple intersystem crossing channels from the

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singlet to triplet transitions in Cd_2L_2 $(S_1 \rightarrow T_2 \sim T_7)$.^[11] This is favorable for the population of triplet exciton states, and accounts for the generation of RTP and LPL in Cd_2L_2 , which is absent in pure organic ligand. Summing up the above experimental and theoretical results, we can deduce a proposed energy transfer mechanism for Cd_2L_2 as illustrated in Scheme 1: first, the metal-organic supramolecules absorb UV/WL/NIR light energy *via* either OPA or TPA pathway, and transfer to the excited singlet states S_n , which can emit blue fluorescence. Or otherwisely, S_n states transit to the excited triplet states T_n *via* intersystem cross, which then emit orange phosphorescence. And additionally, T_n states further relax to lower-energy T_n' states after ceasing of light radiation, leading to the unique LPL phenomenon triggered by UV/WL/NIR light in Cd_2L_2 .



Figure 4. a) Schematic diagrams of TD-DFT energy levels and possible ISC channels of Cd_2L_2 . b-e) Demonstration models for applying Cd_2L_2 in b) camouflaging, c) anti-counterfeiting, d) decorating, and e) displaying.

The above multiple photophysical and especially unique LPL emissions of Cd₂L₂ can be applied in different directions. Based on the naked-eye yellow color under daylight, blue emission under 365 or 780 nm excitation, white light emission under 405 nm excitation, and red LPL emission after removing different kinds of light source, the stripes of a chameleon (Figure 4b), the logo of "School of Chemistry" (Figure 4c), as well as the mascot of "Sun Yat-Sen University" (Figure 4d), can behave various kinds of color images by changes in outer irradiation. These can represent for the application models in camouflaging, anticounterfeiting, and decorating, respectively. Furthermore, by the combination of non-LPL HTzDPTpy ligand (L) and LPL Cd₂L₂, a multiple displaying panel can be established. Under the radiation of UV or NIR light, both L and Cd₂L₂ emit blue luminescence, and therefore, the patterned numbers are non-distinguishable between the two kinds of mosaics, and display blue light "8888". While after turning off the radiation, only Cd2L2-patterned mosaics can give red LPL, and appear as "2018" instead.

In summary, a M₂L₂ metal-organic supramolecular box has been successfully designed to possess multiple photophysical attributes. Single phase white light and dual emissions comprised of blue fluorescence and orange RTP (room temperature phosphorescence) can be reached by adjusting the excitation wavelength and temperature. OPA and TPA properties of the D-π-A type ligand are well inherited by the supramolecular box. And most importantly, LPL (long persistent luminescence) can be triggered by wideband irradiation from UV, WL to NIR light source via either OPA or TPA pathway. This study brings forward a novel strategy to combine TPA with LPL together, and successfully implements the idea of TPA-LPL for the first time. The delicate design of such kinds of metal-organic supramolecular assemblies provides a universal reservior of UV, WL to NIR light energy for the persuit of LPL and other optical potentials to be applicable in wide fields.

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Keywords: LPL • metal-organic box • TPA • white light• NIR

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By delicate design of D- π -A ligand bearing both one-photon absorption (OPA) and two-photon absorption (TPA) attributes, LPL can be triggered in the assembled metal-organic supramolecular box by all wavebands from UV, WL to NIR region, via either OPA or TPA pathways.



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Page No. – Page No.	ge No.	- Page	e No.
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