

# Front end for the model and its Output

AI Paper Review & Summary

localhost:8501

Deploy

AI System to Automatically Review and Summarize Research Papers

Upload Research PDFs

Drag and drop files here  
Limit 200MB per file • PDF

Browse files

pubs1.pdf 3.1MB

Normalized Text Preview

Processed Content

ABSTRACT: Micro-cocrystals of the intermolecular charge-transfer (CT) complex formed from pyrene and tetracyanobenzene can be fabricated via a solution-based method. Intersystem crossing of the directly excited CT exciton in the cocrystal is observed, yielding a CT triplet exciton that undergoes efficient triplet-triplet energy transfer to a diphenylanthracene (DPA)-based triplet acceptor. For the first time, we demonstrate that these micro-cocrystals can act as triplet sensitizers to upconvert the emission of liquid-state DPA triplet acceptors, enabling highly efficient triplet-triplet annihilation photon upconversion (TTA-UC) from 532 to 430 nm. This work demonstrates the utilization of CT excitons as triplet sensitizers in a TTA-UC process, providing a novel approach for efficient and heavy-atom-free UC systems. P. photon upconversion (UC) via triplet-triplet annihilation (TTA) is an emerging photophysical process that enables conversion of low-energy photons to higher-energy emissions under low-power, noncoherent excitation. 1-5 This mechanism offers significant potential for applications in solar energy harvesting, 6-8 photocatalysis, 9-11 bioimaging, 12 and photodynamic therapy. 10 The TTA-UC system operates through sequential energy transfer processes mediated by two key components: a triplet sensitizer and an annihilator. Upon absorption of incident photons, the sensitizer undergoes intersystem crossing (ISC) to populate its triplet state; subsequent triplet-triplet energy transfer (TTET) to the annihilator generates triplet-excited annihilators. Finally, the collision of two triplet annihilators via TTA produces one singlet-excited annihilator, which decays radiatively to emit upconverted fluorescence. To date, most sensitizers employed in TTA-UC systems are heavy-metal complexes owing to their high ISC efficiency. 13 However, significant research efforts have been directed toward developing heavy-atom-free organic triplet sensitizers, motivated by their advantageous properties including reduced toxicity, lower production costs, and enhanced biocompatibility. 14,15 In addition to the conventional spin-orbit coupling mediated ISC mechanism, two alternative pathways for triplet state generation have been identified in organic donor-acceptor systems: 16 radical pair intersystem crossing (RPISC) 17 and spin-orbit charge transfer intersystem crossing (SOCT-ISC). 18,19 In RP-ISC, sufficient spatial separation between donor and acceptor moieties reduces spin-spin exchange interactions, enabling ISC within radical pairs. Conversely, SOCT-ISC occurs in closely spaced, orthogonally configured donor-acceptor systems where charge transfer induces orbital angular momentum changes that offset spin angular momentum variations to conserve the total angular momentum. It is widely accepted that SOCT-ISC typically occurs in intramolecular systems where donor (D) and acceptor (A) adopt an orthogonal configuration and is unlikely to occur in intermolecular charge-transfer (CT) cocrystals that exhibit a nonorthogonal cofacial  $\pi$ - $\pi$  stacking motif. Recently, Wasielewski's group reported SOCT-ISC in cofacial  $\pi$ -stacked cocrystal

Generate Summary & Review

Paper Summary

16°C  
Partly cloudy

Search

ENG  
IN

23:31  
09-01-2026

AI Paper Review & Summary

localhost:8501

Deploy

Generate Summary & Review

Paper Summary

To date, most sensitizers employed in TTA-UC systems are heavy-metal complexes owing to their high ISC efficiency. 13 However, significant research efforts have been directed toward developing heavy-atom-free organic triplet sensitizers, motivated by their advantageous properties including reduced toxicity, lower production costs, and enhanced biocompatibility. 14,15 In addition to the conventional spin-orbit coupling mediated ISC mechanism, two alternative pathways for triplet state generation have been identified in organic donor-acceptor systems: 16 radical pair intersystem crossing (RPISC) 17 and spin-orbit charge transfer intersystem crossing (SOCT-ISC). 18,19 In RP-ISC, sufficient spatial separation between donor and acceptor moieties reduces spin-spin exchange interactions, enabling ISC within radical pairs. Experimental details, kinetics analysis details, and photophysical properties of pyrene and TCNB (PDF) ■ AUTHOR INFORMATION Corresponding Authors Jianlei Han – College of Biological and Chemical Engineering, Jiaxing University, Jiaxing 314001, China; orcid.org/0000-0001-6566-7621; Email: hanjianlei@jxu.edu.cn Pengfei Duan – Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China; University of Chinese Academy of Sciences, Beijing 101408, China; orcid.org/0000-0002-5971-7546; Email: duanpf@nanoctr.cn Zihao Xu – Beijing National Laboratory for Molecular Sciences, Huairou Research Center, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; orcid.org/0000-0003-0805-8533; Email: zhaohu@iccas.ac.cn Authors Zhiying Bai – Beijing National Laboratory for Molecular Sciences, Huairou Research Center, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China Jiao Mu – Beijing National Laboratory for Molecular Sciences, Huairou Research Center, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China Xue Jin – Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China Xuefeng Yang – Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China; orcid.org/00090001-9921-0176 Tongshan Zhao – Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China Yonghong Shi – Xi'an Rare Metal Materials Institute Co., Ltd., Northwest Institute for Non-ferrous Metal Research, Xi'an 710016, China Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.5c17410> Notes The authors declare no competing financial interest. ■ ACKNOWLEDGMENTS This work was supported by National Natural Science Foundation of China (22588301, 22405215, 22302046, 22205045, 22172041, 52173159, 92356307, and 22403097), the National Key Basic R&D Research Program of Ministry of Science and Technology of the People's Republic of China (2021YFA1200303), and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB0960000, XDB0960200, XDB0960201). ISC, Triplet, and TTET Lifetime  $\tau_{ISC} = 1 \pm \text{TTET triplet} = 1 \pm \text{TTET 2 QY TTET} 22.3 \pm 2.8 \text{ ns } 89.6 \pm 9.3 \text{ ns } 0.582 \pm 0.011 \mu\text{s } 79.5 \pm 23.9 \mu\text{s } 86.6 \pm 9.0\%$  Figure 4. (a) FLIM and (b) fluorescence image of CT cocrystals 1 covered by a drop of annihilator 2 in air excited by 532 nm with the collected emission from 440 to 470 nm. (c) FLIM and (d) fluorescence of 2 under the same excitation and detection conditions show no observable fluorescence (sparkies are due to the instrument response to the scattered excitation), ruling out the direct excitation of the annihilator. the American Chemical Society pubs.acs.org/JACS Communication <https://doi.org/10.1021/jacs.5c17410> J. A large crystal of 1 is prepared so that the probe beam Figure 1. (a) Chemical structures of CT sensitizer complex 1 composed of pyrene-TCNB and 9,10-diphenylanthracene-based liquid annihilator 2. (b) Normalized absorption and emission spectra of the powder of 1 ( $\lambda_{ex} = 360 \text{ nm}$ ) and the liquid film of 2 ( $\lambda_{ex} = 360 \text{ nm}$ ) between two quartz glasses. (c) HOMOMO and (d) LUMO diagrams of 1. (e) Spin density distribution of the CT cocrystal on the electron donor pyrene and electron acceptor TCNB in the triplet state. (f) Outline of the CT exciton sensitized TTA-UC process. P. photon upconversion (UC) via triplet-triplet annihilation (TTA) is an emerging photophysical process that enables conversion of low-energy photons to higher-energy emissions under low-power, noncoherent excitation. 1-5 This mechanism offers significant potential for applications in solar energy harvesting, 6-8 photocatalysis, 9-11 bioimaging, 12 and photodynamic therapy. 10 The TTA-UC system operates through sequential energy transfer processes mediated by two key components: a triplet sensitizer and an annihilator. The highest occupied molecular orbital (HOMO) is exclusively localized on the pyrene donor moiety (Figure 1 c), while the lowest unoccupied molecular orbital (LUMO) resides entirely on the TCNB acceptor (Figure 1 d), facilitating CT excitation through electron promotion from the donor HOMO to the acceptor LUMO. 26 This strong CT transition manifests as a new visible absorption band centered at 500 nm (Figure 1 b), lower than that of pyrene or TCNB (Figure S2 b). Moreover, Dexter energy transfer, which relies on electron exchange between triplet states (e.g., TTET between sensitizers and annihilators, or TTA of annihilators), typically occurs over extremely short ranges ( $<1 \text{ nm}$ ). 23 Here, we report, to the best of our knowledge, the first example of a CT exciton-sensitized upconversion process in a liquid annihilator matrix, enabling efficient triplet energy transfer at the solid-liquid interface.

Abstract

ABSTRACT: Micro-cocrystals of the intermolecular charge-transfer (CT) complex formed from pyrene and tetracyanobenzene can be fabricated via a solution-based method.

Results

Although upconversion quantum yield could not be determined due to challenges in quantifying absorbed photons, these results, to the best of our knowledge, provide the first experimental demonstration of CT exciton utilization in TTAUC systems

16°C  
Partly cloudy

Search

ENG  
IN

23:31  
09-01-2026

The screenshot shows a web browser window with the address bar displaying 'localhost:8501'. The page content is divided into sections: 'Abstract', 'Results', and 'Limitations'. The 'Abstract' section describes the synthesis of a micro-co-crystal complex from pyrene and tetracyanobenzene. The 'Results' section discusses the photophysical properties and the mechanism of triplet energy transfer. The 'Limitations' section mentions the challenges in quantifying absorbed photons. The browser interface includes a search bar, navigation icons, and a taskbar at the bottom showing various applications and system status.

[illegible]