

Visible-to-UV Photon Upconversion in Nanostructured Chromophoric Ionic Liquids

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This article is dedicated to the 80th birthday of Professor Jean-Marie Lehn.

Visible-to-ultraviolet (vis-to-UV) triplet-triplet annihilation based photon upconversion (TTA-UC) is achieved in a non-volatile chromophoric ionic liquid (IL) for the first time. A novel IL is synthesized by combining UV-emitting anion 4-(2-phenyloxazol-5-yl)benzenesulfonate (PPOS) and trihexyltetradecylphosphonium cation (P_{66614}). The nanostructured organization of chromophoric anions is demonstrated by synchrotron X-ray and optical measurements. When the IL is doped with a triplet sensitizer tris(2-phenylpyridinato)iridium(III) ($\text{Ir}(\text{ppy})_3$), the visible-to-UV TTA-UC with a relatively low threshold excitation intensity of 61 mW cm^{-2} is achieved. This is due to a large triplet diffusion coefficient in the IL ($1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) as well as a high absorption coefficient 15 cm^{-1} and a long PPOS triplet lifetime of 1.55 ms, all implemented in the condensed IL system. This work demonstrates the unique potential of ILs to control chromophore arrangements for desired functions.

The flourishing of the chemistry based on molecular self-assembly provided a new perspective in soft condensed materials and caused a rise of functional design even in liquids.^[1] The controlled organization of chromophoric moieties in such condensed soft matters is essential for advanced optical and optoelectronic functions. In this respect, ionic liquids (ILs) are particularly of interest because of the unique bicontinuous nanostructures consisted of polar and nonpolar domains.^[2]

Such a unique bicontinuous structure of ILs allows the controlled accumulation of functional units for desired functions.^[3]

Recent progress in photon upconversion based on triplet-triplet annihilation (TTA-UC; Figure S1) has opened a new avenue of photon energy utilization in many areas including biological applications.^[4,5] The typical mechanism of TTA-UC includes multiple Dexter energy transfer processes of donor-to-acceptor triplet energy transfer (TET) and inter-acceptor TTA. Although TTA-UC has been extensively investigated and optimized for the visible wavelength range, the visible-to-ultraviolet (vis-to-UV) TTA-UC is more difficult despite its importance for boosting the efficiency of photocatalysis and artificial photosynthesis.^[6] For example, a threshold excitation intensity (I_{th}) is related to a required excitation intensity for achieving the half of maximum UC quantum yield, which serves as a figure of merit of the TTA-UC systems.^[7] Most of the reported vis-to-UV TTA-UC systems show high I_{th} over several W cm^{-2} with only a few exceptions below 100 mW cm^{-2} .^[6c,d] This is mainly due to the short triplet lifetime of acceptors, inefficient triplet sensitization, or small absorption coefficient. Thus, the development of low-power vis-to-UV TTA-UC molecular systems remains an outstanding issue.

In this work, we report the first IL that exhibits vis-to-UV TTA-UC (Figure 1a). We have recently reported the green-to-blue TTA-UC with low I_{th} in chromophoric ILs, where the acceptor chromophore arrays in the nonpolar IL domain allow effective triplet exciton diffusion.^[3a,b] Based on this concept, we designed a new IL composed of flexible alkyl-chained cation trihexyltetradecylphosphonium (P_{66614}) and UV-emitting anion 4-(2-phenyloxazol-5-yl)benzenesulfonate (PPOS) (Figure 1b). Tris(2-phenylpyridinato)iridium(III) ($\text{Ir}(\text{ppy})_3$)-doped IL P_{66614} PPOS showed a vis-to-UV TTA-UC emission with a low I_{th} value below 100 mW cm^{-2} , demonstrating the notable performance of self-assembled chromophoric ILs.

NaPPOS was synthesized by sulfonation of PPO. The position of the sulfonate group was confirmed by ^1H NMR spectroscopy and single-crystal X-ray analysis (Figure S2).^[8] Subsequent ion-exchange with $P_{66614}\text{Cl}$ gave the UV/blue fluorescent IL P_{66614} PPOS (Figure 2a, b), of which the purity was confirmed by elemental analysis and ^1H NMR spectroscopy. A polarized microscopy image of P_{66614} PPOS showed no birefringence, confirming the absence of crystalline components (Figure 2c). A differential scanning calorimetry (DSC) thermogram of P_{66614} PPOS showed a glass transition at around -44°C

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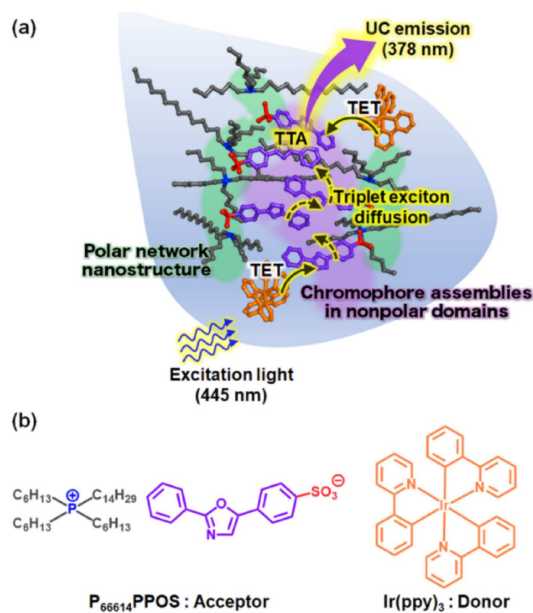


Figure 1. (a) Schematic illustration of vis-to-UV TTA-UC by triplet exciton diffusion in the IL $P_{66614}PPOS$ doped with $Ir(ppy)_3$. (b) Chemical structures of acceptor $P_{66614}PPOS$ and donor $Ir(ppy)_3$.

without any exothermic/endothermic peak (Figure S3). These results identify that $P_{66614}PPOS$ forms the IL phase at room temperature. This was also supported by the absence of sharp peaks in its synchrotron powder X-ray diffraction (PXRD) pattern (Figure 2d). The PXRD pattern also indicated the existence of the bicontinuous network nanostructures in $P_{66614}PPOS$ composed of polar ionic and nonpolar alkyl/chromophore domains.^[2,3a,b] The low-angle peak at 2.7° of $P_{66614}PPOS$ was in accordance with those of the precursor IL $P_{66614}Cl$ and our previous blue-emitting chromophoric IL having the same P_{66614} cation.^[3a] The distance of 1.75 nm corresponds to the separation between the ionic domains, which is mainly determined by the size of the bulky cation.^[3a,b]

In order to evaluate the chromophore assembly structure in the nanostructured $P_{66614}PPOS$, absorption and fluorescence spectra were obtained (Figure 2e). A red-shifted broad absorption band of the neat IL $P_{66614}PPOS$ compared with that of the 0.01 mM DMF solution of $P_{66614}PPOS$ indicates the electronic interactions between neighboring PPOS in the neat state. The small wavelength shift in the fluorescence spectra of neat IL compared with that of the DMF solution is favorable for TTA-UC with a maximum anti-Stokes shift.

$P_{66614}PPOS$ in DMF solution showed a single-exponential fluorescence decay with a lifetime of 1.32 ns (Figure S4). On the other hand, that of the neat IL $P_{66614}PPOS$ was deconvoluted into three components, 0.267 ns (28%), 1.00 ns (62%), and 6.34 ns (10%) with an averaged fluorescent lifetime of 1.34 ns. This multicomponent fluorescence decay would be due to the occasionally-formed strongly interacting sites, which is not surprising for condensed systems.^[3a,b] The fluorescence quantum yields Φ_{FL} of the neat IL and 0.01 mM DMF solution of $P_{66614}PPOS$ were 37.0% and 99.3%, respectively. The smaller Φ_{FL}

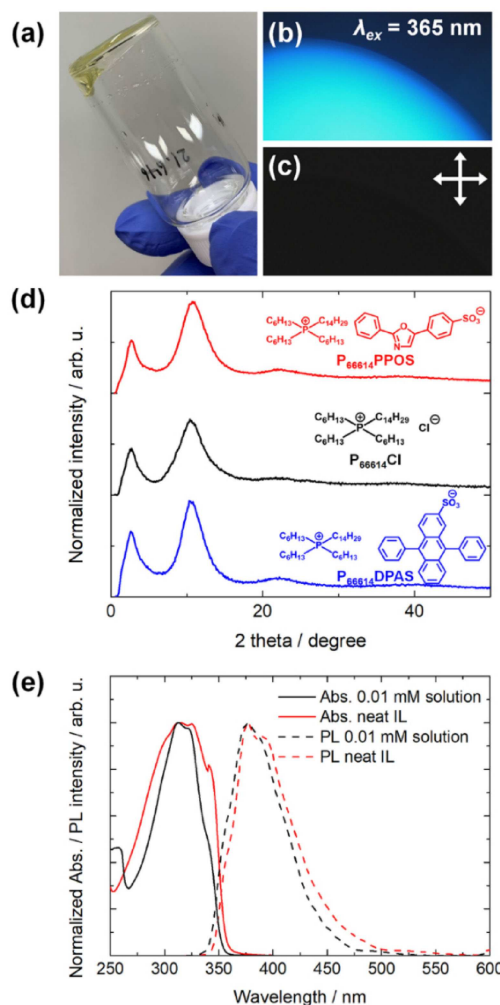


Figure 2. (a) Picture of IL $P_{66614}PPOS$ in a glass vial. (b) Optical microscopic image of IL $P_{66614}PPOS$ under UV irradiation ($\lambda_{ex} = 365$ nm). (c) Birefringent optical microscopic image of IL $P_{66614}PPOS$. (d) Synchrotron X-ray diffraction patterns of $P_{66614}PPOS$ (red), the precursor IL $P_{66614}Cl$ (black), and the previously reported chromophoric IL $P_{66614}DPAS$ (blue). (e) UV-vis absorption (solid lines) and photoluminescence (PL, dashed lines) spectra of 0.01 mM DMF solution of $P_{66614}PPOS$ (black) and neat $P_{66614}PPOS$ (red).

in the IL state is due to the decrement of the radiative decay constant (k_r) and the increment of the nonradiative decay constant (k_{nr}) associated with the formation of quenching sites for singlet excitons in the condensed IL state (Table S2).

$Ir(ppy)_3$ was employed as the triplet donor since its triplet energy level (2.4 eV) is slightly higher than that of PPO (2.3 eV), which facilitates the triplet energy transfer (TET). Upon irradiating 445 nm blue continuous-wave laser, the 0.1 mol% $Ir(ppy)_3$ -doped $P_{66614}PPOS$ showed an upconverted UV/blue emission with a peak at 378 nm (Figure 3a). The position of the emission peak was identical to that of the fluorescence emission peak of IL $P_{66614}PPOS$ (378 nm, Figure 2e). The achieved anti-stokes shift of 0.49 eV is larger than those of our previously reported green-to-blue upconverting ILs (0.42 eV).^[3a,b] The upconversion quantum yield (Φ_{UC}) of the IL $P_{66614}PPOS$ was 0.44% at an excitation intensity (I_{ex}) of 5.0 W cm^{-2} . This efficiency is lower than the Φ_{UC} observed for a DMF solution containing $Ir(ppy)_3$ (0.1 mM) and

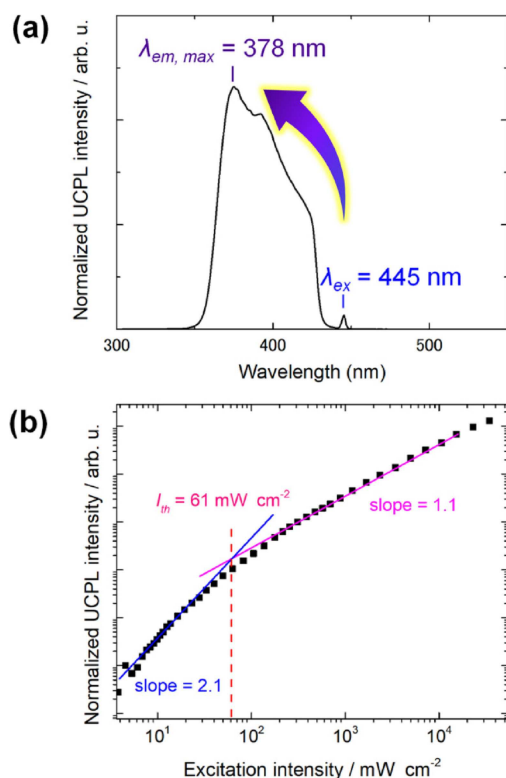


Figure 3. (a) TTA-UC emission spectrum of neat P₆₆₆₁₄PPOS doped with 0.1 mol% Ir(ppy)₃ ($\lambda_{ex} = 445$ nm, 425 nm short-pass filter). (b) Double-logarithm plot of TTA-UC emission intensity of neat IL P₆₆₆₁₄PPOS against the incident light power density.

P₆₆₆₁₄PPOS (10 mM) (5.2% at $I_{ex} = 50$ W cm⁻²) and the Φ_{UC}' values of solvent-free vis-to-UV UC systems with the similar anti-Stokes shift reported by Ma and co-workers (2.6%⁶⁹ and 0.69%^{6j}). From the phosphorescence quantum yield of Ir(ppy)₃, the efficiency of donor-to-acceptor TET (Φ_{TET}) in the IL and that in the DMF solution was estimated to 76% and 79%, respectively (see Experimental methods in SI for details). Considering the similar Φ_{TET} observed for these specimens, the decreased Φ_{UC}' in the IL system would be ascribed to the smaller Φ_{FL} and promoted singlet back energy transfer (BET) in the IL state. The BET quantum yield (Φ_{BET}) was evaluated as 31% by analyzing the fluorescence lifetimes of neat P₆₆₆₁₄PPOS with and without Ir(ppy)₃ (Figure S5). Triplet excitons may also be trapped at the strongly-interacting sites, as observed previously for the chromophoric IL.^[3b]

Significantly, a relatively low I_{th} value of 61 mW cm⁻² was observed in the donor-doped IL (Figure 3b), which was much smaller than that of the mixed DMF solution of Ir(ppy)₃ and P₆₆₆₁₄PPOS (512 mW cm⁻²; Figure S6). The I_{th} is described as below,^[9]

$$I_{th} = (8\pi a_0 \alpha \Phi_{TET} D_T)^{-1} \tau_T^{-2} \quad (1)$$

where a_0 , α , D_T and τ_T represent the effective TTA distance, absorption coefficient, the triplet diffusion coefficient, and the acceptor triplet lifetime. The acceptor triplet lifetimes were

1.55 ms and 0.976 ms for the neat IL and the DMF solution, respectively (Figure S7). The longer lifetime in the IL P₆₆₆₁₄PPOS would be due to the suppression of the chromophore mobility in the condensed viscous environment. Another advantage of the condensed IL system is the larger absorption coefficient of $\alpha = 15$ cm⁻¹ compared with that in solution (0.70 cm⁻¹). The triplet diffusion coefficient of the neat IL system was also calculated according to equation (1). The a_0 of PPO molecule was estimated as 0.75 nm by measuring the TTA-UC properties of a model system; non-substituted 2,5-diphenyloxazole (PPO) and Ir(ppy)₃ in deaerated DMF (Experimental methods, SI). The calculated D_T in neat IL P₆₆₆₁₄PPOS was 1.4×10^{-7} cm² s⁻¹, which is only one order of magnitude smaller than the molecular diffusion coefficient of PPO in DMF (4.1×10^{-6} cm² s⁻¹). This large triplet exciton diffusion constant is obtained by virtue of the densely organized chromophores in the IL nanostructure.

In conclusion, we demonstrate the first example of chromophoric IL exhibiting vis-to-UV TTA-UC. The UV-emitting chromophores are densely assembled in nonpolar nanodomains of the IL. Furthermore, the low I_{th} value is achieved in the IL thanks to the elongated triplet lifetime, the high absorption coefficient and the large triplet exciton diffusion coefficient. These features demonstrate the new potential of nanostructured chromophoric ILs for advanced excitonic functions and their applications to UV-induced reactions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: functional supramolecular chemistry · self-assembly · nanostructures · ionic liquids · photon upconversion

- [1] a) M. J. Hollamby, M. Karny, P. H. H. Bomans, N. A. J. M. Sommerdijk, A. Saeki, S. Seki, H. Minamikawa, I. Grillo, B. R. Pauw, P. Brown, J. Eastoe, H. Möhwald, T. Nakanishi, *Nat. Chem.* **2014**, *6*, 690–696; b) S. S. Babu, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3950–3953; c) F. Lu, E. A. Neal, T. Nakanishi, *Acc. Chem. Res.* **2019**, *52*, 1834–1843; d) V. C. Wakchaure, L. V. Pillai, Goudappagouda, K. C. Ranjeesh, S. Chakrabarty, S. Ravindranathan, P. R. Rajamohanam, S. S. Babu, *Chem. Commun.* **2019**, *55*, 9371–9374; e) A. Shinohara, C. Pan, L. Wang, T. Nakanishi, *Mol. Syst. Des. Eng.* **2019**, *4*, 78–90.
- [2] a) J. N. A. C. Lopes, A. A. H. Pádua, *J. Phys. Chem. B* **2006**, *110*, 3330–3335; b) A. Triolo, O. Russina, H.-J. Bleif, E. D. Cola, *J. Phys. Chem. B* **2007**, *111*, 4641–4644; c) M. G. D. Pópolo, G. A. Voth, *J. Phys. Chem. B* **2004**, *108*, 1744–1752; d) A. Triolo, O. Russina, B. Fazio, R. Triolo, E. D. Cola, *Chem. Phys. Lett.* **2008**, *457*, 362–365; e) T. Pott, P. Méléard, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5469–5475; f) S. Patra, A. Samanta, *J. Phys. Chem. B* **2012**, *116*, 12275–12283; g) V. Migliorati, A. Serva, G. Aquilanti, S. Pascarelli, P. D'Angelo, *Phys. Chem. Chem. Phys.* **2015**, *17*, 16443–16453; h) D. Majhi, M. Sarkar, *Phys. Chem. Chem. Phys.* **2017**, *19*, 23194.
- [3] a) S. Hisamitsu, N. Yanai, N. Kimizuka, *Angew. Chem. Int. Ed.* **2015**, *54*, 11550–11554; *Angew. Chem.* **2015**, *127*, 11712–11716; b) S. Hisamitsu, N.

- Yanai, H. Kouno, E. Magome, M. Matsuki, T. Yamada, A. Monguzzi, N. Kimizuka, *Phys. Chem. Chem. Phys.* **2018**, *20*, 3233–3240; c) X. Mao, P. Brown, C. Cervinka, G. Hazell, H. Li, Y. Ren, D. Chen, R. Atkin, J. Eastoe, I. Grillo, A. A. H. Padua, M. F. C. Gomes, T. A. Hatton, *Nat. Mater.* **2019**, DOI: 10.1038/s41563-019-0449-6
- [4] a) S. Balushev, V. Yakutkin, G. Wegner, B. Minch, T. Miteva, G. Nelles, A. Yasuda, *J. Appl. Phys.* **2007**, *101*, 023101; b) T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573; c) J. Z. Zhao, S. Ji, H. Guo, *RSC Adv.* **2011**, *1*, 937–940; d) J. H. Kim, J. H. Kim, *J. Am. Chem. Soc.* **2012**, *134*, 17478–17481; e) Y. C. Simon, C. Weder, *J. Mater. Chem.* **2012**, *22*, 20817–20830; f) K. Börjesson, D. Dzebo, B. Albinsson, K. Moth-Poulsen, *J. Mater. Chem. A* **2013**, *1*, 8521–8524; g) A. Nattestad, Y. Y. Cheng, R. W. MacQueen, T. F. Schulze, F. W. Thompson, A. J. Mozer, B. Fückel, T. Khoury, M. J. Crossley, K. Lips, G. G. Wallace, T. W. Schmidt, *J. Phys. Chem. Lett.* **2013**, *4*, 2073–2078; h) V. Gray, D. Dzebo, M. Abrahamsson, B. Albinsson, K. Moth-Poulsen, *Phys. Chem. Chem. Phys.* **2014**, *16*, 10345–10352; i) S. H. C. Askes, A. Bahreman, S. Bonnet, *Angew. Chem. Int. Ed.* **2014**, *53*, 1029–1033; *Angew. Chem.* **2014**, *126*, 1047–1051; j) M. Häring, R. Pérez-Ruiz, A. J. von Wangelin, D. D. Díaz, *Chem. Commun.* **2015**, *51*, 16848–16851; k) R. Andernach, H. Utzat, S. D. Dimitrov, I. McCulloch, M. Heaney, J. R. Durrant, H. Bronstein, *J. Am. Chem. Soc.* **2015**, *137*, 10383–10390; l) T. F. Schulze, T. W. Schmidt, *Energy Environ. Sci.* **2015**, *8*, 103–125; m) J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, *Chem. Rev.* **2015**, *115*, 395–465; n) D. Di, L. Yang, J. M. Richter, L. Meraldi, R. M. Altamimi, A. Y. Alyamani, D. Credgington, K. P. Musselman, J. L. MacManus-Driscoll, R. H. Friend, *Adv. Mater.* **2017**, *29*, 1605987; o) Z. Huang, M. L. Tang, *J. Am. Chem. Soc.* **2017**, *139*, 9412–9418; p) S. P. Hill, K. Hanson, *J. Am. Chem. Soc.* **2017**, *139*, 10988–10991; q) J. Park, M. Xu, F. Li, H.-C. Zhou, *J. Am. Chem. Soc.* **2018**, *140*, 5493–5499; r) B. D. Ravetz, A. B. Pun, E. M. Churchill, D. N. Congreve, T. Rovic, L. M. Campos, *Nature* **2019**, *565*, 343–346; s) N. Kimizuka, Y. Sasaki, M. Oshikawa, P. Bharmoria, H. Kouno, A. Hayashi-Takagi, M. Sato, I. Ajioka, N. Yanai, *Angew. Chem. Int. Ed.* **2019**, DOI: 10.1002/anie.201911025
- [5] a) N. Yanai, N. Kimizuka, *Chem. Commun.* **2016**, *52*, 5354–5370; b) A. Monguzzi, M. Ballabio, N. Yanai, N. Kimizuka, D. Fazzi, M. Campione, F. Meinardi, *Nano Lett.* **2018**, *18*, 528–534; c) D. Yang, P. Duan, M. Liu, *Angew. Chem. Int. Ed.* **2018**, *57*, 9357–9361; *Angew. Chem.* **2018**, *130*, 9501–9505; d) X. Yang, J. Han, Y. Wang, P. Duan, *Chem. Sci.* **2019**, *10*, 172–178; e) B. Joarder, N. Yanai, N. Kimizuka, *J. Phys. Chem. Lett.* **2018**, *9*, 4613–4624; f) V. Gray, K. Moth-Poulsen, B. Albinsson, M. Abrahamsson, *Coord. Chem. Rev.* **2018**, *362*, 54–71; g) T. Ogawa, M. Hosoyamada, B. Yurash, T. Q. Nguyen, N. Yanai, N. Kimizuka, *J. Am. Chem. Soc.* **2018**, *140*, 8788–8796; h) T. Ogawa, N. Yanai, S. Fujiwara, T.-Q. Nguyen, N. Kimizuka, *J. Mater. Chem. C* **2018**, *6*, 5609–5615; i) S. Amemori, R. K. Gupta, M. L. Böhm, J. Xiao, U. Huynh, T. Oyama, K. Kaneko, A. Rao, N. Yanai, N. Kimizuka, *Dalton Trans.* **2018**, *47*, 8590–8594.
- [6] a) W. Zhao, F. N. Castellano, *J. Phys. Chem. A* **2006**, *110*, 11440–11445; b) T. N. Singh-Rachford, F. N. Castellano, *J. Phys. Chem. A* **2009**, *113*, 5912–5917; c) F. Deng, J. Blumhoff, F. N. Castellano, *J. Phys. Chem. A* **2013**, *117*, 4412–4419; d) P. Duan, N. Yanai, N. Kimizuka, *Chem. Commun.* **2014**, *50*, 13111–13113; e) M. Majek, U. Faltermeier, B. Dick, R. Pérez-Ruiz, A. J. Wangelin, *Chem. Eur. J.* **2015**, *21*, 15496–15501; f) N. Yanai, M. Kozue, S. Amemori, R. Kabe, C. Adachi, N. Kimizuka, *J. Mater. Chem. C* **2016**, *4*, 6447–6451; g) X. Jiang, X. Guo, J. Peng, D. Zhao, Y. Ma, *ACS Appl. Mater. Interfaces* **2016**, *8*, 11441–11449; h) J. Peng, X. Guo, X. Jiang, D. Zhao, Y. Ma, *Chem. Sci.* **2016**, *7*, 1233–1237; i) V. Gray, P. Xia, Z. Huang, E. Moses, A. Fast, D. A. Fishman, V. I. Vullev, M. Abrahamsson, K. Moth-Poulsen, M. L. Tang, *Chem. Sci.* **2017**, *8*, 5488–5496; j) Q. Chen, Y. Liu, X. Guo, J. Peng, S. Garakyaraghi, C. M. Papa, F. N. Castellano, D. Zhao, Y. Ma, *J. Phys. Chem. A* **2018**, *122*, 6673–6682; k) K. Okumura, N. Yanai, N. Kimizuka, *Chem. Lett.* **2019**, *48*, 1347–1350; l) S. He, X. Luo, X. Liu, Y. Li, K. Wu, *J. Phys. Chem. Lett.* **2019**, *10*, 5036–5040.
- [7] A. Monguzzi, R. Tubino, S. Hoseinkhani, M. Campione, F. Meinardi, *Phys. Chem. Chem. Phys.* **2012**, *14*, 4322–4332.
- [8] CCDC 1948169 (NaPPOS)
- [9] A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, F. Meinardi, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *78*, 195112.

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