Photoresponsive aggregation-induced emission polymer film for anti-counterfeiting

Hong Yang , Mengqi Li , Weijun Zhao , Zhiqian Guo ,
Wei-Hong Zhu

PII: S1001-8417(21)00366-1
DOI: https://doi.org/10.1016/j.cclet.2021.05.053
Reference: CCLET 6396

To appear in: *Chinese Chemical Letters*

Please cite this article as: Hong Yang , Mengqi Li , Weijun Zhao , Zhiqian Guo , Wei-Hong Zhu , Photoresponsive aggregation-induced emission polymer film for anti-counterfeiting, *Chinese Chemical Letters* (2021), doi: https://doi.org/10.1016/j.cclet.2021.05.053

Communication

Photoresponsive aggregation-induced emission polymer film for anti-counterfeiting

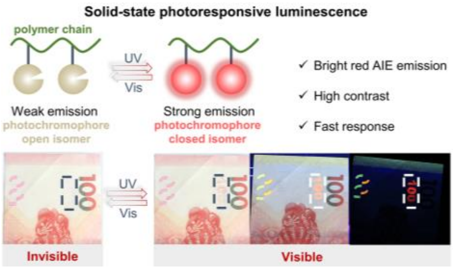
Hong Yang, Mengqi Li, Weijun Zhao*, Zhiqian Guo, Wei-Hong Zhu

Shanghai Key Laboratory of Functional Materials Chemistry, Key Laboratory for Advanced Materials and Institute of Fine Chemicals, Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Shanghai 200237, China

∗ Corresponding author.
E-mail address: zhwj@ecust.edu.cn (W. Zhao).

∗ Corresponding author.
E-mail address: zhwj@ecust.edu.cn (W. Zhao).

Graphical Abstract



Integrating steric-hindrance diarylethene into flexible polymer chains enables reversibly solid-state photochromism and excellent AIE activity. Such fascinating polymer film with phototransformation between invisible and visible is successfully established in anti-counterfeiting.

ABSTRACT

The development of solid-state smart materials, in particular those showing photoresponsive luminescence, is highly desirable for their cutting edge applications in displays, sensors, data-storage, and anti-counterfeiting. However, to achieve both excellent photoresponsive performance and bright luminescence in solid state remains challenge. Herein, we integrate a novel photochromic fluorophore YL into flexible polymer chains, thereby enabling the resultant polymer PYL with reversible photoisomerization upon aggregation. Remarkably, the polymer PYL possesses excellent photochromic properties and aggregation-induced emission (AIE) activity, which can be attributed to the photoactive YL moiety. Upon light exposure, its film exhibits reversibly off-to-on fluorescent modulation with quick response, high emission efficiency and signal contrast, sharply different from the weak emission in solution. The novel photoresponsive AIE polymer with invisible/visible color and fluorescence transformation allows for advanced anti-counterfeiting applications. This work provides an efficient platform for constructing solid-state photocontrollable luminescent materials.

Keywords:

Aggregation-induced emission; Photoresponsive luminescence; Diarylethene; Photochromism; Polymer film; Anti-counterfeiting

Solid-state smart materials with stimulus responsive luminescence have attracted increasing attention for a variety of applications, such as displays [1-3], environmental monitoring [4-6], bio-imaging [7-9], and anti-counterfeiting [10-12]. Of particular interest are those photoresponsive luminescent materials, as light is more attractive to realize high-precise spatiotemporal control in a non-invasive way [13-15]. As the most widely utilized photoresponsive units, diarylethenes are capable of undergoing reversible photo-triggered structural isomerization with fast response, excellent thermal bistability and fatigue resistance [16-19]. Although encoding fluorophores into diarylethenes has been widely utilized to achieve photo-induced fluorescence regulation [20-22], this strategy always faced with complicated synthetic route and unavoidable trade-off between fluorescence and photochromic properties [23]. And these encoded diarylethenes have limited free space for solid-state photoreactions or faced with aggregation-induced quenched emission which greatly hampers their fluorescent switching in solid state and limits practical applications [24-28].

Recently, our group has developed series of steric-hindrance photochromic systems which possess reversible off-to-on fluorescent photoswitching performance in film with high efficiency and excellent fatigue resistance [29]. But its powder failed to undergo efficient photocyclization reaction mainly since that the rigid environment upon aggregation greatly limited the intermolecular space [30]. The doped method indeed provided more free volume to afford the photocyclization process, but would easily bring uneven dispersion without isotropy and precipitation by crystallization. Instead, covalently linking photochromophore to flexible polymer chains can not only address the above problems, but also make the resultant polymer possesses good processability [31-34], which is conducive to the further practical application.

Accordingly, we here incorporated steric-hindrance photochromic unit YL into flexible polymer chains through radical copolymerization (Fig. 1). The resultant polymer PYL displayed both excellent aggregation-induced emission (AIE) and reversibly photoresponsive properties in solid state with high photocyclization quantum yield, thermal bistability and fatigue resistance. Upon UV/visible light irradiation, PYL film exhibits reversibly off-to-on fluorescent and obvious color switching with quick response and high contrast. Such polymer film and its fascinating photoresponsive color and luminescent properties allow high-tech applications in advanced anti-counterfeiting.

As the reported photochromic core compound BBTE has photoactive antiparallel (*ap*-) and photoinactive parallel (*p*-) conformers which were successfully separated [35], we synthesized pure *ap*-YL and *p*-YL by the Suzuki coupling reaction (Scheme S1 in Supporting information). Indeed, the conversion between *ap*-YL and *p*-YL was totally blocked (Scheme S2 in Supporting information) under room temperature, according to the NMR spectra. All chemical structures were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as high-resolution mass spectra (HRMS). Then, the target polymer PYL (Scheme S1) was obtained by the radical polymerization of photoactive *ap*-YL and NIPAM unit. With polystyrene as a standard and THF as solvent, the number-average molecular weight M_n and polydispersity M_w/M_n of PYL is 40428 and 1.58 (Fig. S18 in Supporting information), respectively, measured by GPC, indicative of a narrow molecular weight distribution. The molar ratio of photochromic moiety and NIPAM units was about 1: 907, calculated from the absorption spectra (Fig. S19 in Supporting information) [36,37].

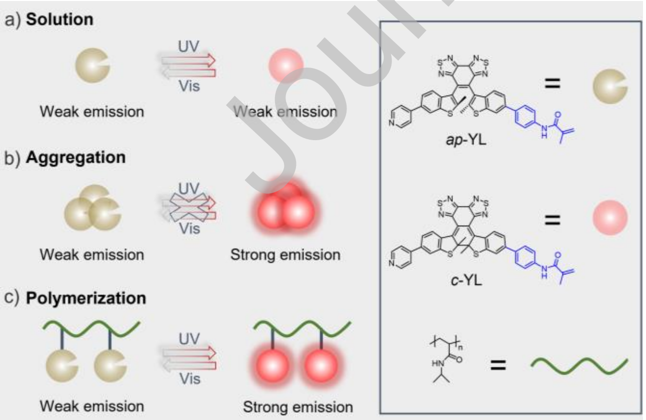


Fig. 1. Design strategy of photoresponsive AIE polymer. Light-modulated luminescence switching of photochromophores in different states, including the photoactive monomer YL (a) in solution, (b) in aggregate state, and (c) polymer PYL in aggregate sate. The structure of photoresponsive unit YL and polymer unit are shown on the right.

In case of photochromic diarylethenes, only *ap*-conformer can undergo photocyclization reaction from open to closed isomer [38,39], thus we studied the photoswitching behavior of *ap*-YL and *p*-YL individually in solution. As expected, pure *p*-YL showed neither absorption nor emission change upon light irradiation (Fig. S20 in Supporting information). In contrast, the initial colorless THF solution of *ap*-YL turned red accompanied by a new absorption band centered at 552 nm (Fig. 2a), which is identical to its closed isomer (*c*-). The photocyclization conversion ratio was up to 98% (Table S1 in Supporting information). Meanwhile, we noticed that *ap*-YL in THF solution displayed weak fluorescence centered at 544 nm (Table S2 in Supporting information), resulting from the intramolecular charge transfer process due to its donor-*π*-acceptor structure. This emission gradually quenched until reaching photostationary state (*pss*-). And then under visible light (λ > 510 nm), it totally returned to the initial state with recovered emission. During this reversible process, the photocyclization and photocycloreversion quantum yield was 0.70 and 0.05, respectively. In addition, YL showed excellent thermal bistability at 293 K and 318 K, and can undergo 10 cycles upon alternative UV and visible light irradiation without obvious decay (Figs. S21-S23 in Supporting information). Such results revealed that *ap*-YL underwent reversibly and efficiently on-to-off fluorescent switching upon light irradiation with excellent thermal bistability and fatigue resistance.

Then we checked the photochromic behavior of polymer PYL in solution (Fig. 2b, Table S1, Figs. S21-S23). As depicted in Fig. 2b, the absorption and emission curve of polymer PYL is similar to that of its photochromic monomer. Upon UV irradiation, the THF solution of PYL turned from colorless to red along with a new broad absorption band centered at 554 nm, indicative of the transformation from open to closed isomer. Meanwhile, its initial emission centered at 561 nm gradually quenched with red-shifted wavelength. Until reaching the photostationary state, the photocyclization conversion ratio was up to 95%. Similar to monomer YL, PYL displayed outstanding thermal stability and fatigue resistance (Figs. S21-S23). It can be concluded that after polymerization, the polymer still possesses excellent photoresponsive properties with on-to-off fluorescent switching in solution.

Traditional fluorescent photochromic system always faces the problem of the aggregation-caused quenching, which greatly limited its practical application. Thus we further checked the fluorescent properties of both monomer YL and polymer PYL at aggregate state (Figs. 2c and d, Figs. S24 and S25 and Table S2 in Supporting information).

As depicted in Fig. 2c, the emission spectra of open isomers *ap*-YL and *ap*-PYL in THF/H_2O mixtures with different water fraction were measured to investigate their AIE behavior. *ap*-YL showed weak emission in pure THF with a fluorescence quantum yield of 1.04% (Fig. 2c, Table S2). Then with the water fraction increasing from 0 to 60%, the emission gradually decreased accompanied by red-shifted wavelength. Such phenomenon can be ascribed to the D-*π*-A structure of the open isomer, which consists of strong electron acceptor (central benzobisthiadiazole bridge) and strong electron donor (side aryl group) [40-42]. Then the fluorescence restored obviously while water fraction up to 80%, reaching maximal emission efficiency of 3.7%. As for polymer PYL, its open form displayed similar fluorescent behavior in THF/H_2O mixtures to the monomer *ap*-YL. Its emission gradually quenched along with the addition of water into THF, then the fluorescence restored while water fraction over 60%. During this process, its emission efficiency changed from 1.42% in THF to 3.8% in water (Table S2).

As for the closed isomers, *c*-YL displayed weak emission in pure THF. And then upon the addition of water, its emission increased sharply accompanied with fluorescence quantum yield from 0.12% to 11.2% (Fig. 2c, Table S2). Then considering the difficulty in obtaining the closed isomer of PYL and the high conversion ratio (95%) of photocyclization reaction, we observed the fluorescent properties of *pss*-PYL in THF/H_2O mixtures instead (Fig. 2d). Similar to monomer *c*-YL, *pss*-PYL displayed excellent AIE characteristic with the fluorescent quantum yield from 0.44% to 10.5% (Table S2).

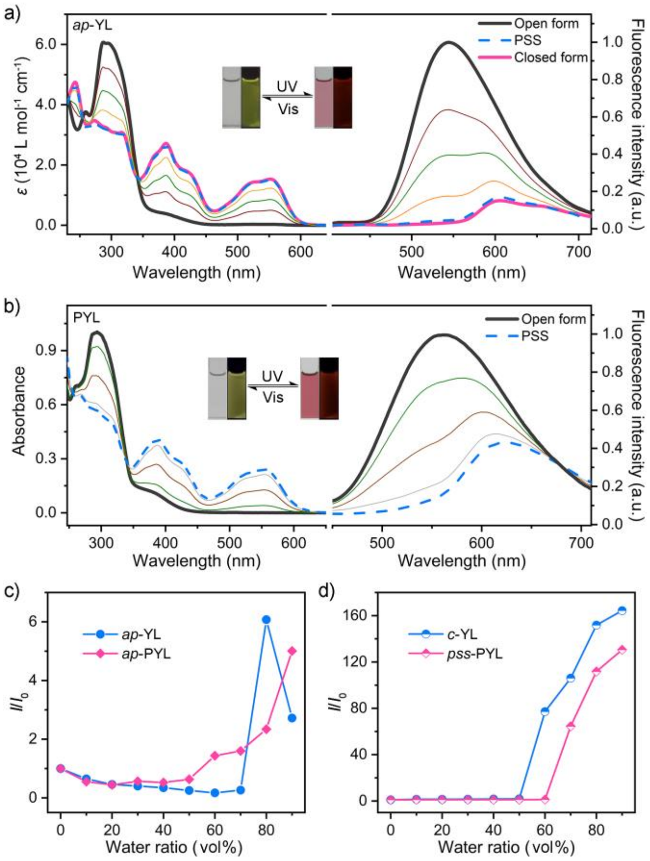


Fig. 2. Photochromic and AIE properties of monomer *ap*-YL and polymer PYL. Absorption and fluorescence spectra of (a) monomer *ap*-YL (2.0×10^{-5} mol/L) and (b) polymer PYL (1.80 g/L) in THF upon UV irradiation at 313 ± 10 nm. Excitation for fluorescence of monomer and polymer is set at isobestic point at 341 and 343 nm, respectively. Inset images in (a) and (b) show the color and emission changes of monomer and polymer, respectively. (c) Relative fluorescence intensity I/I_0 plots of open isomers *ap*-YL (2.0×10^{-5} mol/L) and *ap*-PYL (1.0 g/L) in THF/H_2O mixtures with different water ratios, excited by 341 and 343 nm, respectively. (d) Relative fluorescence intensity I/I_0 plots of closed isomers *c*-YL (2.0×10^{-5} mol/L) and *pss*-PYL (1.0 g/L) in THF/H_2O mixtures with different water ratios, excited by 552 and 554 nm, respectively. Here, I is the fluorescence intensity with different water ratios, and I_0 is initial fluorescence intensity in pure THF.

The excellent AIE properties of both YL and PYL motivated us to further explore their photoswitching fluorescence in solid state. Firstly, given that the powder of YL failed to undergo photocyclization reaction, the fluorescent switching upon light irradiation was tested in aggregated state (THF/H_2O = 2/8, v/v, Fig. S26 in Supporting information). Upon visible light irradiation (λ > 510 nm), the initial strong emission of *c*-YL gradually decreased (Fig. S26a), indicating that *c*-YL in aggregated state can undergo photocycloreversion reaction to the open form. However, after that, with continuous UV irradiation, the emission appeared negligible changes (Fig. S26b), indicating that the open isomer failed to undergo photocyclization reaction, consistent with the photoinduced performance of YL powder. This result revealed that monomer YL can only undergo irreversible light-driven fluorescent switching upon aggregation. Such behavior may be attributed to that the rigid environment upon aggregation greatly limited the intermolecular space, thus failing to afford the photocyclization process (Fig. 1) [30,35].

In contrast, it was discovered that PYL powder displayed reversible photoswitching under alternative UV and visible light irradiation (Fig. 3a and Fig. S25). Before UV exposure, the color of PYL powder was pale yellow with a broad emission band around 500-600 nm. Then under irradiation by a hand-held ultraviolet lamp (λ = 365 ± 20 nm), the color gradually changed to dark red along with red-shifted emission (641 nm), corroborating the photo-induced conversion from open to closed isomer. During this process, its emission switched with a high contrast ratio (fluorescence efficiency increased from 6.1% to 24.0%). Then continuous visible light irradiation (λ > 510 nm) can drive the red powder convert back to the initial pale color state. Such reversible photoswitching of polymer PYL, different from that of monomer, can be ascribed to that after polymerization, the environment around the photochromic moiety became softer, thereby bringing enough space to afford efficient photocyclization reaction.

Accordingly, given that the closed isomer of polymer PYL showed strong red emission in solid state, we further investigated the photoinduced fluorescent changes of PYL film, expecting to achieve turn-on fluorescent switching (Fig. 3). Here, the polymer film was prepared by coating THF solution with polymer PYL (30 wt%) on the top of quartz glass under room temperature, with a thickness of 1.05 μm (Fig. S27 in Supporting information). Firstly, the color of this film was pale yellow, along with negligible emission excited by 554 nm due to negligible absorption (Fig. 3b). Then upon UV (λ = 365 ± 20 nm) exposure, the pale yellow color of PYL film turned red immediately. Simultaneously, its emission displayed obvious enhancement, which can be ascribed to the conversion from open to closed isomer. After that, under visible light (λ > 510 nm) exposure, such emission centered at 645 nm gradually decreased and finally converted back to the initial state, accompanied by the obvious color changing from bright red to pale yellow (Fig. 3c). Notably, the contrast ratio of fluorescent signal was up to 177 during this cycle. And upon alternative UV and visible light exposure, little decay occured even after 11 cycles (Fig. 3d). SEM photos also indicated that there were no obvious defects before and after light exposure for PYL film (Fig. S28 in Supporting information). Accordingly, the polymer PYL film exhibited efficiently and reversibly off-to-on fluorescent switching upon light irradiation with excellent fatigue resistance and high signal contrast.

Advances in thin-film technology have enabled a wide range of breakthroughs in the areas of flexible display, optical coating, and energy storage. Our polymer film material PYL exhibits excellent photoresponsive luminescence and AIE performance which was further demonstrated in anti-counterfeiting (for the detailed preparation procedure, see the Supporting Information). As shown in Fig. 4, the number “100” was readily coated on the blank area of a banknote by THF solution with polymer PYL (10 wt%), and the coated area was almost invisible under room light. While upon UV light ($\lambda = 365 \pm 20$ nm) irradiation, the red number “100” quickly appeared in the coated area within 0.1 s, accompanied with bright red emission, thus the number turning to visible. Notably, such strong emission can be clearly observed under both room light and UV light. Then, under visible light ($\lambda > 510$ nm) irradiation, the emission and color of “100” gradually faded out and reverted to the initial invisible state. Also, the polymer PYL can be well attached to wine bottle. Similarly, the emblem figure coated on the bottle quickly changed from invisible to red with clear outline upon UV irradiation, along with bright red emission, and then returned to the invisible state under visible light exposure. Such photocontrollable performance between invisible and visible state successfully verified the application of polymer PYL in anti-counterfeiting.

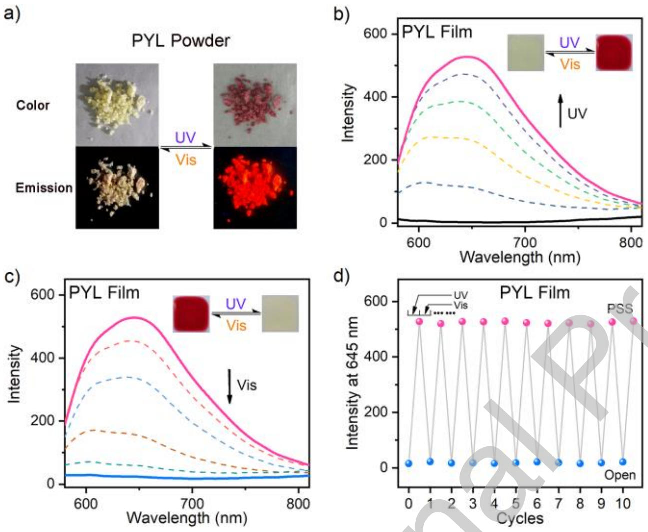


Fig. 3. Fluorescent switching of polymer PYL in solid powder and film. (a) Room light (up) and fluorescent (down) pictures of PYL powder under UV ($\lambda = 365 \pm 20$ nm) and visible light ($\lambda > 510$ nm) irradiation, in which the fluorescent pictures were recorded under UV light ($\lambda = 365 \pm 20$ nm). Fluorescence spectra of PYL film upon (b) UV light ($\lambda = 365 \pm 20$ nm; 0, 0.5, 1.5, 3.5, 6.5, and 10 s) and (c) visible light ($\lambda > 510$ nm; 0, 5, 15, 45, 90, and 150 s), excited at 554 nm. Inset images showed the color changes of film before and after UV irradiation. (d) Fatigue resistance of fluorescence intensity at 645 nm upon alternative UV ($\lambda = 365 \pm 20$ nm) and visible light ($\lambda > 510$ nm) irradiation for PYL film.

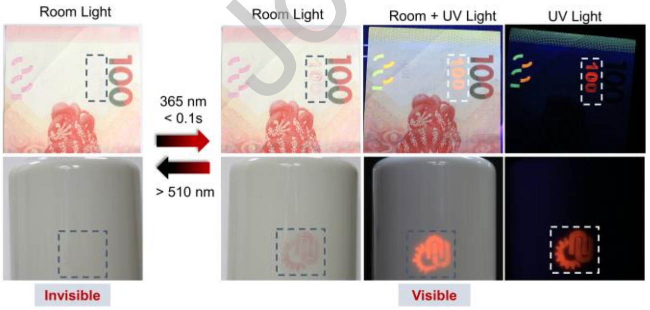


Fig. 4. Application of photoresponsive AIE polymer film in anti-counterfeiting. The photoinduced color and emission changes between invisible and visible transformation on a banknote (up) and wine bottle (down) coated with PYL. The color pictures were recorded under room light, and the fluorescent pictures were recorded under UV light ($\lambda = 365 \pm 20$ nm).

In this work, a novel photocontrollable fluorescent polymer PYL with excellent AIE activity is constructed *via* encoding steric-hindrance photochromic fluorophore YL into flexible polymer chains. After polymerization, polymer PYL possesses excellent photoresposive properties and AIE activity inherit from monomer YL, and meanwhile successfully provides requisite free space for efficient photocyclization reaction in aggregate state. In solution, both the open and closed isomer of PYL exhibit weak emission. In contrast, the open isomer of PYL shows weak color and fluorescence while its closed isomer exhibits bright red color and fluorescent emission in solid state. Upon alternative UV and visible light irradiation, both its powder and film successfully realize reversibly off-to-on photoresponsive color and fluorescent switching with quick response and high contrast. Such fascinating photoresponsive polymer film are well coated on banknote and wine bottle, exhibiting reversibly invisible/visible both color and fluorescent information, indicative of its promising application in photo controllable anti-counterfeiting.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China for Science Center Program (No. 21788102), Creative Research Groups (No. 21421004) and Key Project (No. 21636002), Shanghai Pujiang Program (No. 20PJ1402900), and National key Research and Development Program (No. 2016YFA0200300), Shanghai Municipal Science and Technology Major Project (No. 2018SHZDZX03), and Program of Introducing Talents of Discipline to Universities (No. B16017).

References

[1] T. Grotjohann, I. Testa, M. Leutenegger, et al., Nature 478 (2011) 204-208.

[2] D. Okada, Z.H. Lin, J.S. Huang, et al., Mater. Horiz. 7 (2020) 1801-1808.

[3] J. Liang, M. Chu, Z. Zhou, et al., Nano Lett. 20 (2020) 7116-7122.

[4] J. Dong, K. Zhang, X. Li, et al., Nat. Commun. 8 (2017) 1142.

[5] Y. Yang, S. Zhang, X. Zhang, et al., Nat. Commun. 10 (2019) 3165.

[6] X. Jiang, H. Gao, X. Zhang, et al., Nat. Commun. 9 (2018) 3799.

[7] D. Kim, K. Jeong, J.E. Kwon, et al., Nat. Commun. 10 (2019) 3089.

[8] L. Zong, H. Zhang, Y. Li, et al., ACS Nano 12 (2018) 9532-9540.

[9] H. Wu, Z. Chen, W. Chi, et al., Angew. Chem. Int. Ed. 58 (2019) 11419-11423.

[10] Z. Li, X. Liu, G. Wang, et al., Nat. Commun. 12 (2021) 1363.

[11] Y. He, J. Li, J. Li, et al., ACS Appl. Polym. Mater. 1 (2019) 746-754.

[12] Z. Li, G. Wang, Y. Ye, et al., Angew. Chem. Int. Ed. 58 (2019) 18025-18031.

[13] P. Wei, J.X. Zhang, Z. Zhao, et al., J. Am. Chem. Soc. 140 (2018) 1966-1975.

[14] D. Kim, J.E. Kwon, S.Y. Park, Adv. Funct. Mater. 28 (2018) 1706213.

[15] F.D. Jochum, P. Theato, Chem. Soc. Rev. 42 (2013) 7468-7483.

[16] K. Uno, M.L. Bossi, M. Irie, et al., J. Am. Chem. Soc. 141 (2019) 16471-16478.

[17] G. Naren, C.W. Hsu, S. Li, et al., Nat. Commun. 10 (2019) 3996.

[18] J. Zhang, Y. Fu, H.H. Han, et al., Nat. Commun. 8 (2017) 987.

[19] Y. Takagi, T. Kunishi, T. Katayama, et al., Photochem. Photobiol. Sci. 11 (2012) 1661.

[20] X. Wu, Z. Zhang, H. Liu, S. Pu, RSC Adv. 10 (2020) 15547-15553.

[21] S. Tang, F. Song, M. Lu, et al., Sci. China Chem. 62 (2019) 451-459.

[22] Z. Xu, Q.T. Liu, X. Wang, et al., Chem. Sci. 11 (2020) 2729-2734.

[23] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 114 (2014) 12174-12277.

[24] C. Li, H. Yan, L.X. Zhao, et al., Nat. Commun. 5 (2014) 5709.

[25] T. Fukaminato, T. Doi, N. Tamaoki, et al., J. Am. Chem. Soc. 133 (2011) 4984-4990.

[26] J.W. Chung, S.J. Yoon, S.J. Lim, et al., Angew. Chem. Int. Ed. 48 (2009) 7030-7034.

[27] X. Zhang, D. Görl, V. Stepanenko, F. Würthner, Angew. Chem. Int. Ed. 53 (2014) 1270-1274.

[28] L. Ma, C. Li, Q. Yan, et al., Chin. Chem. Lett. 31 (2020) 361-364.

[29] H. Yang, M. Li, C. Li, et al., Angew. Chem. Int. Ed. 59 (2020) 8560-8570.

[30] G. Liu, S. Pu, R. Wang, Org. Lett. 15 (2013) 980-983.

[31] H. Nie, J.L. Self, A.S. Kuenstler, et al., Adv. Opt. Mater. 7 (2019) 1900224.

[32] Z. Wang, Z. Ma, Y. Wang, et al., Adv. Mater. 27 (2015) 6469-6474.

[33] Y. Gu, E.A. Alt, H. Wang, et al., Nature 560 (2018) 65-69.

[34] S. Jiang, L. Meng, W. Ma, et al., Chin. Chem. Lett. 32 (2021) 1037-1040.

[35] W. Li, C. Jiao, X. Li, et al., Angew. Chem. Int. Ed. 53 (2014) 4603-4607.

[36] H. Zhou, F. Liu, X. Wang, et al., J. Mater. Chem. C 3 (2015) 5490-5498.

[37] J. Yang, K. Gu, C. Shi, et al., Mater. Chem. Front. 3 (2019) 1503-1509.

[38] M. Irie, Chem. Rev. 100 (2000) 1685-1716.

[39] S. Nakamura, M. Irie, J. Org. Chem. 53 (1988) 6136-6138.

[40] T. Morozumi, T. Anada, H. Nakamura, J. Phys. Chem. B 105 (2001) 2923-2931.

[41] Y. Hong, J.W.Y. Lam, B.Z. Tang, Chem. Commun. (2009) 4332-4353.

[42] L. Meng, X. Ma, S. Jiang, et al., CCS Chem. 3 (2021) 2084-2094.