




Self-contained photo-acid generators with high quantum yields triggered by photo-cyclization†

 Cite this: *Chem. Commun.*, 2022, 58, 13266

 Received 7th September 2022,
 Accepted 26th October 2022

DOI: 10.1039/d2cc04941d

rsc.li/chemcomm

 Zixuan Xu, Zhaoyu Wang, Yanyun Zhang, Xiaokang Yao, Meijuan Ding, Huifang Shi* and Zhongfu An *

We present a novel series of neutral photo-acid generators (PAGs) based on carbazole derivatives. A photo-induced 6π -electrocyclization reaction of carbazole derivatives triggers the subsequent release of halogen acids. With UV irradiation, PAGs spontaneously release acid molecules quantitatively forming polyaromatic compounds. To our knowledge, it is considered the highest quantum yield (over 85%) among Brønsted PAGs.

Photo-acid generators (PAGs) which release various acids upon light irradiation have received extensive attention in recent years owing to their widespread applications, such as micro-lithographic imaging,^{1,2} photocuring,³ 3D printing, cationic polymerization,⁴ and photodynamic therapy,⁵ *etc.* At present, there are mainly two types of PAGs: ionic and non-ionic PAGs.^{6,7} Diphenyllo donium and triarylsulfonium salts are representative ionic PAGs.^{8–12} Non-ionic PAGs, such as *N*-oxy imidesulfonate derivatives have also been applied in photoresists for many years.^{13,14} However, the majority of reported PAGs undergo homolytic bond cleavage reaction after light irradiation, resulting in the generation of photo-generated radical species.^{14,15} These active species need to extract hydrogen atoms from solvent molecules or other hydrogen sources to generate a Brønsted acid.¹² Meanwhile, they are also involved in the photo-redox catalytic reaction, resulting in complicated fragments remaining in the systems.^{16,17} Recently, a number of PAGs that do not require external proton source have been developed, which effectively overcome the above shortcomings of PAGs.^{18–24} For instance, Liao *et al.* reported photo-chromic merocyanine derivatives, which exhibited dynamic photo-isomerization accompanied with changes in acidity.²⁵ Kawai's group has developed a series of efficient PAGs by exploiting the

reactivity of highly sensitive photochromic terarylenes. The terarylene-based PAGs exhibited relatively high photo-chemical quantum yields up to 70%.^{4,26,27} Owing to the quantitative release of alcohols, carboxylic acids, sulfonic acids, and even triflic acid, terarylene-based PAGs were successfully used in the field of polymerizations and organic catalytic reactions.⁴ Sardon's group developed a series of PAGs based on anthrone and anthraquinone, which were able to produce tricarboxylic acid, *p*-toluenesulfonic acid and methanesulfonic acid to trigger ring opening polymerization (ROP) of cyclic esters under 365 nm UV irradiation.²¹ To date, self-contained PAGs still face the problem of a slow photochemical reaction rate and relatively low photo-chemical quantum yields. In addition, these material systems are very limited, which are not conducive to further chemical modification to optimize photophysical properties.

It is well known that carbazole has a strong absorption of ultraviolet light.^{28–35} Moreover, terarylene-based PAGs react at the thiophene group after UV illumination, forming a closed-loop structure and releasing acid. Therefore, we hypothesized that modified halogenated thiophene on carbazole group, might be a new class of self-contained PAGs with fast photo-chemical reaction rate.

Herein, a series of self-contained PAGs were designed and synthesized (CzF, CzCl, and CzBr, Fig. 1). Their chemical structures were characterized by ¹H and ¹³C NMR spectroscopies and mass spectra (Fig. S1–S6 and S11–S13, ESI[†]). Under UV irradiation, they achieved acid generation accompanied with a photochromic behavior. These compounds undergo 6π -electro pericyclization reaction located at hydrogen (H) from carbazole

Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing, 211816, P. R. China. E-mail: iamzf@njtech.edu.cn, iamhfshi@njtech.edu.cn
 † Electronic supplementary information (ESI) available: Experimental section, Fig. S1–S20 and Table S1. CCDC 2203143, 2202708 and 2202707. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2cc04941d>

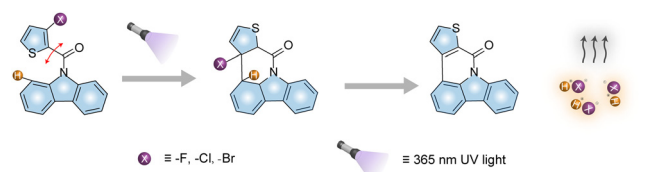


Fig. 1 Photo-acid generation reactions of carbazole derivatives.

group and conjugate base (X) pair from a thiophene group upon photo-irradiation, spontaneously eliminating an acid molecule (HX), producing a structurally stable polycyclic compound (CzC). Moreover, carbazole-based PAGs have good thermal stability and higher photochemical quantum yield ($\Phi > 85\%$). To the best of our knowledge, it is the highest value among the reported self-contained PAGs. Due to the unique photochemical process, this strategy provides a guidance for the subsequent development of PAG materials.

Firstly, the photophysical properties of the carbazole derivatives were studied before and after photo-irradiation. Under irradiation by a 365 nm UV light lamp, the compounds exhibit visual photochromic behaviours.^{36–38} With the extension of irradiation time, the PL spectra of the three compounds changed with the emission intensity at around 390 nm increased obviously, as shown in Fig. S15 (ESI[†]). Impressively, the products after illumination make the pH test paper turn red, indicating the generation of acids (Fig. S16, ESI[†]). Like the photoluminescence behaviour, UV absorption of PAGs varied similarly under the UV irradiation. Without UV light irradiation, there exist peaks at around 305 nm and shoulders at 318 nm for the absorption spectra. With the prolongation of UV irradiation time, new absorption peaks appear at 345 and 365 nm gradually (Fig. 2a–c). It is worth noting that the photo-response rates are very fast, and the chemical equilibriums can be realized within 30 s. The linear fitting curves between irradiation time and absorption intensity shows that the reaction rate of CzF is faster than that of CzCl and CzBr (Fig. 2d). We also characterized the reaction kinetics of CzF by ¹H NMR. Under continuous UV irradiation, a series of new peaks appear at around 7.8, 7.9, 8.1 and 8.8 ppm (Fig. 2e). After purification of the products, we found that it underwent a

6 π -electro cyclization reaction during UV irradiation (Fig. S7, S8, S14 and S17, ESI[†]), resulting in the formation of stable polycyclic compound CzC and halogen acids. At different concentrations, the results show that the concentration of CzC and the absorption intensity exhibit a good linear relationship. The molar absorption coefficient of CzC in THF was calculated to be $(1.45 \pm 0.005) \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ (Fig. 2f). The photochemical quantum yields of CzF, CzCl and CzBr are 93%, 86% and 85% respectively. Subsequently, the thermal stability of PAGs was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC). As shown in Fig. S18a and b (ESI[†]), these PAGs present excellent thermal decomposition temperatures (over 200 °C, Fig. S18b, ESI[†]). The DSC curves reveal that their melting point relationship is CzF > CzCl > CzBr (Fig. S18a, ESI[†]).

To gain insight into the mechanism for acid generation under UV-light irradiation in crystal, the molecular conformations and stacking were investigated through single crystal analysis. All the three compounds showed twisted molecular configurations and the dihedral angles between the carbazole and thiophene planes increased as the halogen atomic radius increases (Fig. 3a–c). Driving by UV light, the molecular rotor rotates to induce that carbazole and the thiophene units are in the same plane. Thus, large closed-loop intermediates are formed, which is beneficial to rapidly release halogen acids.

Additionally, the packing modes of their single crystals are also different. As shown in Fig. 3d–f, the carbazole groups are arranged in parallel and exhibit strong $\pi \cdots \pi$ stacking for CzF. While for CzCl and CzBr, the carbazole groups show zipper arrangement. Therefore, it is reasonably speculated that the more planar the PAG molecules, the smaller the driving force required for rotation, and thus the higher photochemical

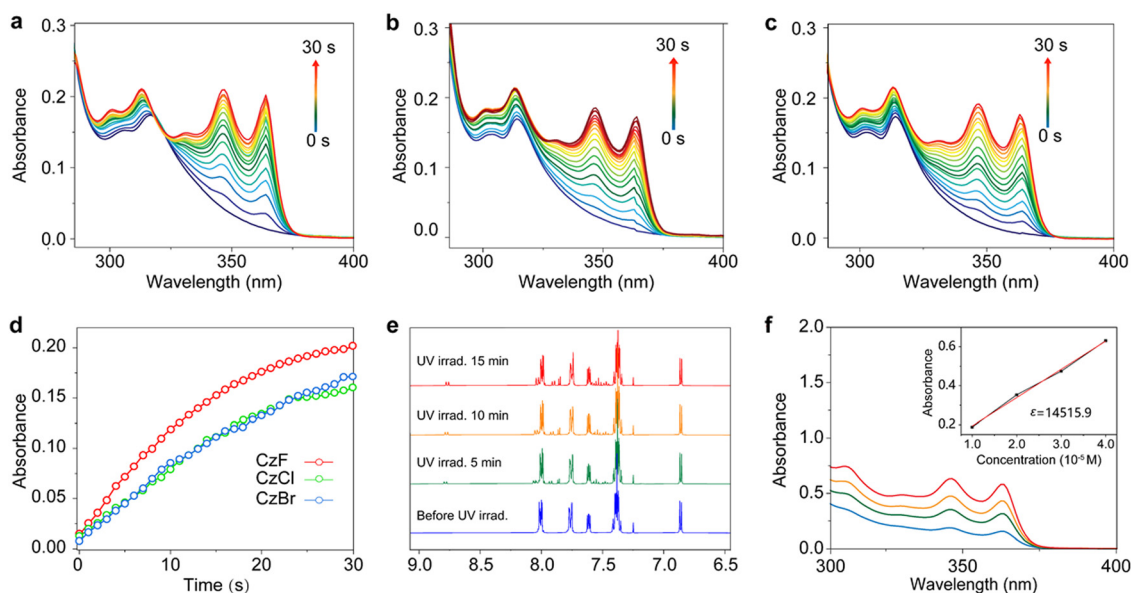


Fig. 2 Absorption spectral change of (a) CzF, (b) CzCl, (c) CzBr by UV (365 nm) irradiation in $(2.0 \times 10^{-5} \text{ M})$ under the ambient conditions. (d) The relationship between absorption intensity at 370 nm for PAGs and UV (365 nm) irradiation time. (e) ¹H NMR spectral change of CzF upon UV (365 nm) irradiation in CDCl₃. (f) Absorption spectra of CzC at different concentrations; (Inset: the relationship between the concentration and absorption intensity at 370 nm for CzC).

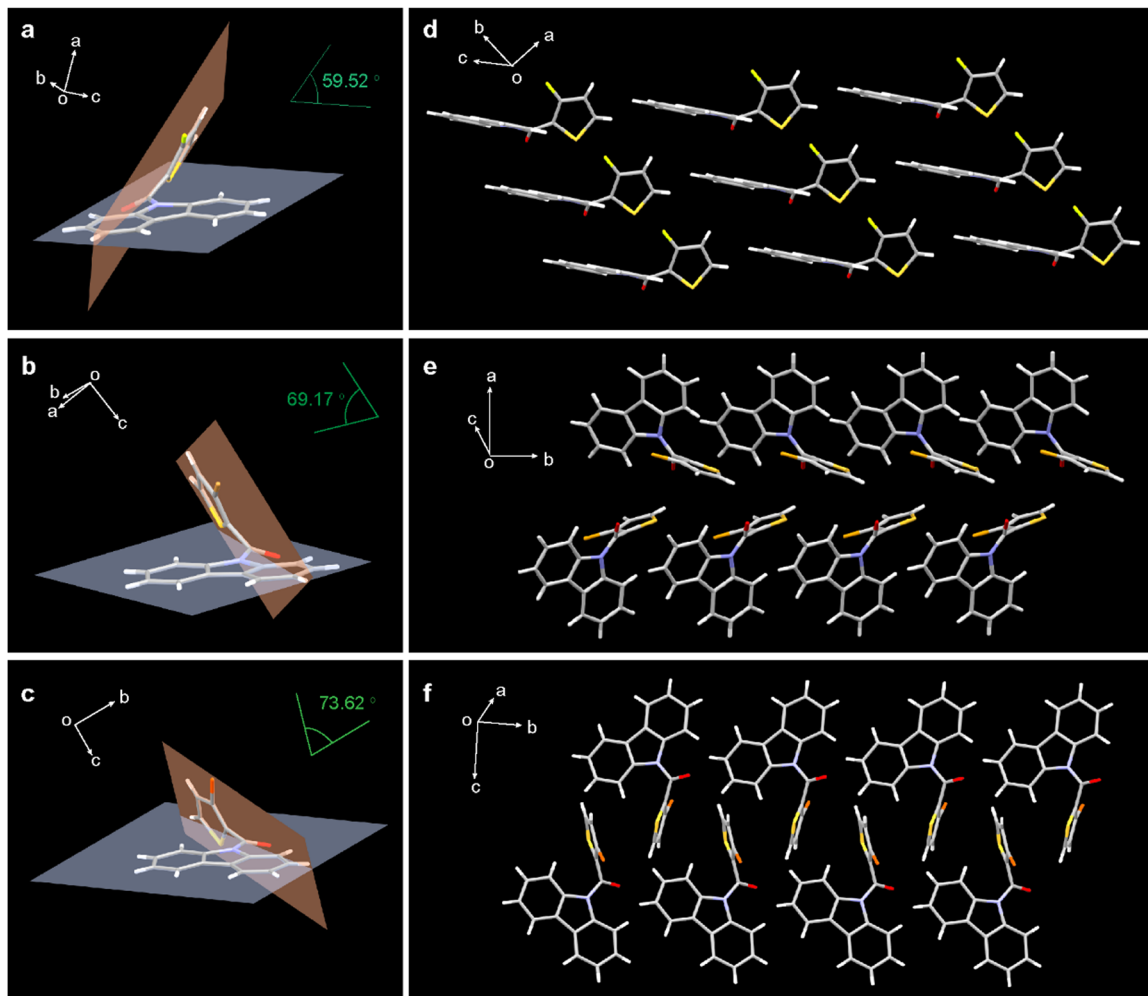


Fig. 3 Probable explanation of different photo-acid quantum yields and melting points. Dihedral Angle between carbazole plane and thiophene plane of (a) CzF, (b) CzCl, and (c) CzBr. The packing modes of crystals of (d) CzF, (e) CzCl, and (f) CzBr.

quantum yield of CzF. Moreover, we carefully analysed the intermolecular interactions in single crystals. In CzF crystal, the molecules were rigidly restricted by C=O \cdots π (3.188 Å), $\pi\cdots\pi$ (3.374–3.385 Å), C-F \cdots H-C (2.616 Å), C-H \cdots π (2.854 Å) interactions, which contribute to restricting molecular motions for good thermo-stability. In comparison, there are fewer molecular interactions in CzCl and CzBr (Fig. S19, ESI †), resulting in less compact molecular packing and lower melting points.

Subsequently, we further conducted a series of control experiment on the mechanism of 6 π -electro pericyclization for acid generation by PAGs. Firstly, we synthesized an isomer of CzBr, named CzBr-2 (Fig. 4a). By analysing the ^1H NMR spectra of CzBr-2 before and after UV irradiation, it was found that their ^1H NMR signals were completely consistent (Fig. 4b), indicating that CzBr-2 did not undergo photochemical reaction. That means the electro pericyclization here is hardly realized due to the strong molecular ring tension of a 7-membered ring. Therefore, we concluded that the substituent position of halogen atom played a decisive role in the photo-acid generation.

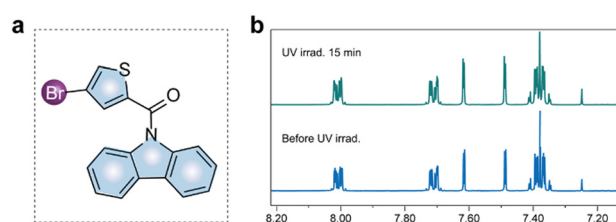


Fig. 4 (a) The chemical structure of contrastive molecule (CzBr-2); (b) ^1H NMR spectral change of CzBr-2 upon UV (365 nm) irradiation in CDCl_3 .

In conclusion, we have successfully designed and synthesized a series of PAGs with high photochemical quantum yields of over 85%. To the best of our knowledge, this is the highest value compared with the reported PAGs (Fig. S20, ESI †). The experimental results proved that these PAGs underwent 6 π -electrocyclization reaction and produced hydrohalic acids under UV illumination.

X-ray single crystal analysis showed that the smaller the dihedral angle between carbazole and thiophene units, the

larger the photo-acid quantum yield. The more intermolecular interactions are, the higher the thermal stability is of the PAGs. This study presents a convenient and effective method to design and synthesize efficient Brønsted PAGs, which will provide a guideline for the study of photo-acid generators in the future.

Financial support from the National Natural Science Foundation of China (Grants No. 21975120, 62134007 and 21875104), the fund for Talented of Nanjing Tech University (No. 201983), and Young Scientific and Technological Talents Project of Jiangsu Association for Science and Technology (JSTJ-2020-026). Jiangsu Postdoctoral Research Funding Program (No. 2021K582C).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 G. M. Wallraff and W. D. Hinsberg, *Chem. Rev.*, 1999, **99**, 1801–1822.
- 2 B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1171–1196.
- 3 J.-P. Fouassier, *Photoinitiation, photopolymerization, and photocuring: fundamentals and applications*, Hanser, 1995.
- 4 T. Nakashima, K. Tsuchie, R. Kanazawa, R. Li, S. Iijima, O. Galangau, H. Nakagawa, K. Mutoh, Y. Kobayashi, J. Abe and T. Kawai, *J. Am. Chem. Soc.*, 2015, **137**, 7023–7026.
- 5 X. Yue, C. O. Yanez, S. Yao and K. D. Belfield, *J. Am. Chem. Soc.*, 2013, **135**, 2112–2115.
- 6 J. V. Crivello, *Adv. Polym. Sci.*, 1984, **62**, 1–48.
- 7 F. Ortica, C. Coenjarts, J. C. Scaiano, H. Liu, G. Pohlers and J. F. Cameron, *Chem. Mater.*, 2001, **13**, 2297–2304.
- 8 J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.*, 1996, **34**, 3231–3253.
- 9 W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, J. K. Cammack, C. K. Ober, J. W. Perry and S. R. Marder, *Science*, 2002, **296**, 1106–1109.
- 10 K. J. Schafer, J. M. Hales, M. Balu, K. D. Belfield, E. W. Van Stryland and D. J. Hagan, *J. Photochem. Photobiol., A*, 2004, **162**, 497–502.
- 11 T. Y. Yu, C. K. Ober, S. M. Kuebler, W. H. Zhou, S. R. Marder and J. W. Perry, *Adv. Mater.*, 2003, **15**, 517–521.
- 12 W. Zhou, S. M. Kuebler, D. Carrig, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 2002, **124**, 1897–1901.
- 13 P. Yang and W. T. Yang, *Chem. Rev.*, 2013, **113**, 5547–5594.
- 14 C. J. Martin, G. Rapenne, T. Nakashima and T. Kawai, *J. Photochem. Photobiol., C*, 2018, **34**, 41–51.
- 15 J. V. Crivello and E. Reichmanis, *Chem. Mater.*, 2014, **26**, 533–548.
- 16 D. A. Nicewicz and D. W. C. MacMillan, *Science*, 2008, **322**, 77–80.
- 17 J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102–113.
- 18 X. Zhang, S. Hu, Q. Ma and S. Liao, *Polym. Chem.*, 2020, **11**, 3709–3715.
- 19 X. Zhang, Q. Ma, Y. Jiang, S. Hu, J. Li and S. Liao, *Polym. Chem.*, 2021, **12**, 885–892.
- 20 N. Guy, O. Giani, S. Blanquer, J. Pinaud and J.-J. Robin, *Prog. Org. Coat.*, 2021, **153**, 106159.
- 21 X. Lopez de Pariza, E. Cordero Jara, N. Zivic, F. Ruipérez, T. E. Long and H. Sardon, *Polym. Chem.*, 2021, **12**, 4035–4042.
- 22 M. J. Supej, E. A. McLoughlin, J. H. Hsu and B. P. Fors, *Chem. Sci.*, 2021, **12**, 10544–10549.
- 23 N. Zivic, P. K. Kuroishi, F. Dumur, D. Gignes, A. P. Dove and H. Sardon, *Angew. Chem., Int. Ed.*, 2019, **58**, 10410–10422.
- 24 M. Valle, M. Ximenis, X. Lopez de Pariza, J. M. W. Chan and H. Sardon, *Angew. Chem., Int. Ed.*, 2022, **61**, e202203043.
- 25 Z. Shi, P. Peng, D. Strohecker and Y. Liao, *J. Am. Chem. Soc.*, 2011, **133**, 14699–14703.
- 26 R. Mizutsu, R. Asato, C. J. Martin, M. Yamada, Y. Nishikawa, S. Katao, M. Yamada, T. Nakashima and T. Kawai, *J. Am. Chem. Soc.*, 2019, **141**, 20043–20047.
- 27 R. Li, T. Nakashima, R. Kanazawa, O. Galangau and T. Kawai, *Chem. – Eur. J.*, 2016, **22**, 16250–16257.
- 28 H. L. Lee, S. O. Jeon, I. Kim, S. C. Kim, J. Lim, J. Kim, S. Park, J. Chwa, W.-J. Son, H. Choi and J. Y. Lee, *Adv. Mater.*, 2022, **34**, 2202464.
- 29 A. Obolda, Q. Peng, C. He, T. Zhang, J. Ren, H. Ma, Z. Shuai and F. Li, *Adv. Mater.*, 2016, **28**, 4740–4746.
- 30 K. Li, Y. Zhu, B. Yao, Y. Chen, H. Deng, Q. Zhang, H. Zhan, Z. Xie and Y. Cheng, *Chem. Commun.*, 2020, **56**, 5957–5960.
- 31 C. Tang, R. Bi, Y. Tao, F. Wang, X. Cao, S. Wang, T. Jiang, C. Zhong, H. Zhang and W. Huang, *Chem. Commun.*, 2015, **51**, 1650–1653.
- 32 F. Lombeck, H. Komber, D. Fazzi, D. Nava, J. Kuhlmann, D. Stegerer, K. Strassel, J. Brandt, A. D. de Zerio Mendaza, C. Müller, W. Thiel, M. Caironi, R. Friend and M. Sommer, *Adv. Energy Mater.*, 2016, **6**, 1601232.
- 33 J. Ouyang, F. Wu, X. Zhao and X. Yang, *Small*, 2022, **18**, 2201769.
- 34 O. G. Poluektov, J. Niklas, K. L. Mardis, S. Beaupré, M. Leclerc, C. Villegas, S. Erten-Ela, J. L. Delgado, N. Martín, A. Sperlich and V. Dyakonov, *Adv. Energy Mater.*, 2014, **4**, 1301517.
- 35 Y. Kawanishi, Y. Segawa, K. Mutoh, J. Abe and Y. Kobayashi, *Chem. Commun.*, 2022, **58**, 4997–5000.
- 36 Y. Li, F. Gu, B. Ding, L. Zou and X. Ma, *Sci. China: Chem.*, 2021, **64**, 1297–1301.
- 37 F. Hu, M. Cao, X. Ma, S. H. Liu and J. Yin, *J. Org. Chem.*, 2015, **80**, 7830–7835.
- 38 W. Miao, S. Wang and M. Liu, *Adv. Funct. Mater.*, 2017, **27**, 1701368.