ChemComm

COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2021, 57, 6546

Received 8th May 2021, Accepted 2nd June 2021

DOI: 10.1039/d1cc02373j

rsc.li/chemcomm

Pillararene-enriched linear conjugated polymer materials with thiazolo[5,4-*d*]thiazole linkages for photocatalysis[†]

Zheng Li, Lu Li, D Yan Wang* and Ying-Wei Yang *

A heteroatom-doped conjugated polymer with tunable bandgap is synthesized using pillararenes as the electron-rich C_2 symmetric nodes and thiazolo[5,4-*d*]thiazole as the electron-deficient linkage. The influence of pillararenes in regulating the band structure and photogenerated charge carrier transportation for photocatalytic environmental contaminant degradation has been revealed.

Photocatalysis has brought ripples of excitement due to its prominent ability to convert solar energy into chemical energy, showing great potential in pollutant degradation, hydrogen evolution, hydrocarbon production, CO2 reduction, and organic transformation.^{1,2} Many photocatalysts including inorganic semiconductors,³ polymeric semiconductors,⁴ metal-organic frameworks,⁵ and covalent organic frameworks (COFs)⁶ were developed to meet the sophisticated requirements of photocatalysis in recent years, as a result of their suitable visible-light absorption and photoelectric properties. However, large band gaps and fast charge recombination could inevitably result in low photocatalytic efficiency and significantly impede their practical applications. Although much effort has been made to break through these restrictions including the introduction of complicated modifications, precise regulation of the band structures and active anchoring sites is still highly desired.⁷ Reticular chemistry has stimulated a tremendous upsurge of interest among the researchers striving to exploit new photocatalysts, because it indicates a clear structure-function relationship and makes modulation feasible on a molecular scale by integrating some appropriate building blocks. A series of porous organic polymers (POPs) such as covalent triazine frameworks, conjugated microporous polymers, and crystalline COFs have been studied especially for use in photocatalysis.8 These porous materials have become recent hot topics due to

their tuneable linking scaffolds and adequate pore windows, and thus exert great influence on materials chemistry.⁹

Supramolecular macrocycles, including crown ethers,10 cyclodextrins,¹¹ calix[n]arenes,¹² cucurbit[n]urils,¹³ and pillar[n] arenes,¹⁴ have occupied important positions in supramolecular and materials chemistry, due to their extraordinary host-guest properties in solution. Among them, pillararenes have been regarded as upcoming synthetic receptors to accommodate specific guests due to their rigid cylinder structures and electron-rich cavities of proper sizes.¹⁵ In addition to the solution-based host-guest chemistry, more and more attention has been paid to pillararenebased supramolecular systems in the solid states more recently, as demonstrated by nonporous adaptive crystals (NACs) that could realize selective uptake and separation in the manner of guestinduced structural or conformational changes.¹⁶ Other than NACs, supramolecular macrocycles such as calixarenes, cyclodextrin, and pillararenes have also attracted particular interest in the construction of functional polymers such as POPs and conjugated macrocycle polymers, in which, macrocyclic compounds not only participate in the fabrication of polymers as crosslinkers, but also offer active anchoring sites from intrinsic pore windows toward targeted molecules and play important roles in regulating the properties of polymers such as adsorption, fluorescence, and catalysis.17 The most concerned feature of pillararenes lies in the fascinating host-guest properties; however, report on the utilization of electron-rich cavities in modulating the behaviour of charge carriers is still rare.

In this work, we designed two kinds of conjugated polymer materials, CP and P5Tz-CP, with terphenyl and diphenylpillararene as the main backbone units, respectively, and both with heterocycle-derived TzTz as the repeating linkages (Scheme 1). Because both the conjugated structure and the heteroatom doping approach are of great strategic importance for enlarging the visible-light absorption range and regulating optoelectronic properties,¹⁸ we envision that the cooperation of synthetic macrocyclic arene and heteroatom doping may modulate the optoelectronic performance and enrich the application of catalysis by rational design.



View Article Online

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China. E-mail: wangy2011@jlu.edu.cn, ywyang@jlu.edu.cn

[†] Electronic supplementary information (ESI) available. CCDC 2065576. For ESI and crystallographic data in CIF or other electronic formats see DOI: 10.1039/ d1cc02373j



 $\label{eq:scheme1} \begin{array}{ll} \mbox{(a) Synthetic routes to P5Tz-CP and CP. (b) Schematic illustration of P5Tz-CP for the photocatalytic degradation of rhodamine B (RhB). \end{array}$

The conjugated polymer with pillararenes as the C_2 symmetric nodes and TzTz units co-doping with nitrogen and sulfur as repeating linkages was synthesized by heating an equivalent amount of dithiooxamide and dibenzaldehydefunctionalized pillar[5]arene (P[5](PhCHO)₂) in anhydrous DMF at reflux (Fig. S1, ESI[†]). P[5](PhCHO)₂ was synthesized based on our published method¹⁷ and its single-crystal structure (CCDC 2065576, Table S1, ESI[†]) suggests that P[5] $(PhCHO)_2$ stacking is stabilized by multiple C-H··· π interactions (C-H··· π distance, 2.828 Å, 2.804 Å) and C-H···O interactions (C-H···O distance, 2.551 Å, 3.189 Å, 3.259 Å) between pillararenes and adjacent pillararenes and/or solvent. P5Tz-CP was obtained as an orange solid in 85% yield. CP was synthesized via the condensation of p-terphenyl-dicarboxaldehyde (TPA) and dithiooxamide in 90% yield. Both polymers are insoluble in water and common organic solvents.

P5Tz-CP and CP were characterized by solid-state ¹³C crosspolarization magic angle spinning (CP-MAS) NMR spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and elemental analysis (Fig. 1). In the ¹³C CPMAS NMR spectra, the peaks at 161 ppm and 168 ppm are attributed to the carbon signals of N=C in the TzTz moieties of CP and P5Tz-CP, respectively, and the weak peak at 155 ppm ascribed to C=C in the TzTz ring of CP indicates the generation of a thiazole ring. The ones located from 110 to 150 ppm belong to the aromatic carbon of TPA and pillararenes. The carbon signals at 55 and 33 ppm could be ascribed to the typical methoxy moiety (-OCH₃) and aliphatic methylene (-CH₂-) of pillararenes. In comparison with the P[5](PhCHO)₂ monomer, carbon signals of aromatic ring in pillararenes and nearby benzene displayed a clear downfield shift of *ca.* 5 ppm, which could be caused by the potential exo-wall interaction of the electron-rich pillararene backbone and the electron-deficient TzTz moieties (Fig. 1a).¹⁵ The peak at ca. 190 ppm indicates the existence of unreacted



Fig. 1 (a) Solid-state CP-MAS 13 C NMR spectra of P5Tz-CP, CP and P[5](PhCHO)₂. (b) FT-IR spectra of TPA (black), P[5](PhCHO)₂ (green), CP (red) and P5Tz-CP (blue). (c) PXRD patterns of P5Tz-CP (black) and CP (red).

aldehyde in CP in line with the result of FT-IR where the aldehyde absorption at ~1695 cm⁻¹ was attenuated in P5Tz-CP and CP. The disappearance of N-H stretching vibration at ~3300 cm⁻¹ further proves the polymerization (Fig. S6, ESI†). Elementary analysis revealed that the content of carbon, hydrogen, nitrogen, oxygen and sulfur agrees well with the theoretical values, for which, slightly higher C, H and O content of CP is attributed to the existence of TPA with unreacted –CHO groups (Table S2, ESI†).

Thermogravimetric analysis (TGA) showed a dramatical decomposition of P5Tz-CP at ca. 400 °C and CP was thermally stable up to 550 °C (Fig. S7, ESI†). Powder X-ray diffraction (PXRD) analysis revealed the amorphous material structure from the broad peaks in the pattern. The porosity has also been measured by N₂ adsorption-desorption at 77 K and CO₂ adsorption-desorption at 273 K. The adsorption isotherm of CP exhibited type II isotherm with a Brunauer-Emmett-Teller (BET) surface area of 41.1124 m² g⁻¹, and the gas sorption experiments revealed P5Tz-CP to be nonporous because of the possible inter-penetration structure between different polymer chains that occupy the spaces. The morphologies of P5Tz-CP and CP were recorded by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images in Fig. 2a indicate the micrometre-scale blocky structure of P5Tz-CP with a convex surface. To monitor the process of the formation of such blocky morphology, we took out a small amount of sample at different polymerization intervals to record the morphology change. As shown in Fig. S9 (ESI⁺), uniform smaller nanorods were found in the initial stage of 12 h, which tend to grow longer and form larger micrometre bulks after 5 d. The stacking layered structure of CP with obvious wrinkles was seen in the TEM and SEM images (Fig. 2d and Fig. S10, ESI⁺), which could facilitate the sufficient contact with substrates in aqueous solutions. From the sheetlike morphology of CP, we deduce that the sharp rise of CP with appreciably increased adsorption quantity under high pressure is caused by condensed macropore along with the stacking of sheet-like structures. The low porosity could be attributed to the twist chains and aggregation of conjugated polymers.

The optoelectronic properties of the conjugated polymers were studied by UV-vis diffuse reflectance spectroscopy (DRS)



Fig. 2 SEM images of (a) P5Tz-CP and (b) CP. TEM images of (c) P5Tz-CP and (d) CP. Elemental mapping shows the contents of N, S, and O for (e) CP and (f) P5Tz-CP.

and photoluminescence spectroscopy (Fig. 3). UV-vis adsorption spectra of both CP and P5Tz-CP showed wide photoabsorption from the UV region to the visible light region up to 700 nm, where the absorption edge of P5Tz-CP exhibits a slight red shift compared with that of CP. Then the ability of charge transfer and separation were assessed by photoluminescence spectroscopy (Fig. S13, ESI⁺), where a much weaker fluorescence intensity of P5Tz-CP is due to the suppressed recombination of photogenerated carriers. The time-resolved photoluminescence spectra showed that the fluorescence lifetime of P5Tz-CP at 580 nm was longer than that of CP, indicating that a more extended electron delocalization existed within the skeleton of P5Tz-CP. These characteristics suggest the superior optoelectronic properties of P5Tz-CP for photocatalysis. Moreover, the band gap energies of P5Tz-CP and CP were calculated to be ca. 1.85 eV and 2.05 eV according to the



Fig. 3 (a) UV-vis adsorption spectra of P5Tz-CP and CP. (b) Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the determination of band gap energy by Kubelka–Munk-transformed reflectance spectra. (c) Time-resolved photoluminescence spectra of P5Tz-CP and CP excited at 400 nm. (d) Band structure of P5Tz-CP and CP.

equation $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where α , $h\nu$, A and E_g represent the absorption coefficient, the photon energy, a constant value, and the band gap energy, respectively.¹⁹ In general, a wider energy band gap indicates higher CB edge positions or lower VB edge positions, accounting for stronger reduction/oxidation abilities of photogenerated e^- and h^+ to improve the photocatalytic activity. As a consequence, by changing the tailorable building blocks, conjugated polymer materials with tuneable band gap can be obtained.

The photocatalytic activity of P5Tz-CP and CP was evaluated by their ability to degrade rhodamine B (RhB) dye under visible light irradiation. Solid catalysts were ground and dispersed into RhB solution (10 mg L^{-1}). The resulting mixtures were continuously stirred in the dark for 1 h to reach an adsorptiondesorption equilibrium. Then, a 300 W Xenon lamp equipped with a 420 nm optical filter was used to irradiate the mixture and the UV-vis absorbance of supernatant solution was measured after various irradiation times to record the RhB degradation efficiency. The degradation processes are summarized in Fig. 4. Compared with the moderate catalytic activity of P5Tz-CP that completely degrades RhB within 4 h in the presence of 0.4 mg mL⁻¹ P5Tz-CP, which is comparable with some reported works,8 CP exhibits better photocatalytic performance (40 min and 0.1 mg mL⁻¹ catalyst concentration), due to the larger contact area with dyes caused by the sheet and aperture structure of CP.

The photocatalytic activity mainly relies on the photo-excited e^- and h^+ , which could react with the surrounding water and oxygen to produce ROS on the catalyst surface, such as superoxide anion radical (${}^{\bullet}O_2^-$), hydroxyl radical (${}^{\bullet}OH$), and singlet oxygen (${}^{1}O_2$), and then prevent the recombination of e^- and h^+ . These generated reactive species are considered to undertake critical missions in the redox reactions with organic pollutants. To explore the functions of ROS involved in the photocatalytic



Fig. 4 UV-vis spectra of RhB upon visible light irradiation at different time intervals in the presence of (a) CP (0.1 mg mL⁻¹) and (b) P5Tz-CP (0.4 mg mL⁻¹). Inset: Photos of RhB solutions during photocatalytic degradation. Scavenger effect on the degradation of RhB in the presence of (c) CP (0.1 mg mL⁻¹) and (b) P5Tz-CP (0.4 mg mL⁻¹) irradiated for 30 min and 2 h, respectively.

process, several controlled experiments were done via adding different scavengers including benzoquinone (BQ, the ${}^{\bullet}O_2^{-}$ scavenger), isopropanol (IPA, the •OH radical scavenger), copper sulfate (CuSO₄, the scavenger for e⁻), disodium ethylenediaminetetraacetate (EDTA-2Na, the scavenger for h⁺), and L-histidine (His, the ${}^{1}O_{2}$ scavenger) separately into the photocatalytic suspension systems under standard reaction conditions. The degradation efficiency calculated using $(((C_0 - C)/C_0) \times 100\%)$, where C_0 and C are the UV-vis absorption of RhB at 554 nm initially and in the process during photocatalysis, was used to evaluate the effects of the scavengers. As shown in Fig. 4, in the case of CP, the addition of BQ and CuSO₄ obviously restrained the degradation efficiency of RhB, indicating that both ${}^{\bullet}O_2^{-}$ and e^{-} play key roles in the photocatalysis process.¹⁸ In terms of P5Tz-CP, ¹O₂, [•]OH, and h⁺ are primarily responsible for photodegradation, suggesting that the predominant redox reactions are different from those of CP, which were caused by the difference of redox ability and band structure. Besides the aerobiotic conditions, identical experiments were also conducted under N2 to remove oxygen, and obvious decrease in the catalytic efficiency was observed for both P5Tz-CP and CP, not only providing an evidence for the significant influence of oxygen as an efficient electron trap for CP, but also indicating the potential of P5Tz-CP as a photosensitizer with light-harvesting ability to realize effective transition from excitation energy to oxygen molecules and then the production of ${}^{1}O_{2}$ for dye degradation.

To better understand the photodegradation mechanism, electrochemical impedance spectroscopy (EIS) and electrochemical Mott-Schottky plots were carried out in a threeelectrode cell. EIS results reveal that P5Tz-CP has a smaller resistance than CP, indicating high carrier mobility caused by the introduction of pillararenes with electron-rich cavities for the improvement of interfacial charge transport ability and photocatalytic properties (Fig. S17, ESI[†]). The positive slope of the Mott-Schottky plots indicates that both conjugated polymers are n-type semiconductors. From Fig. S18, ESI,† the calculated CB potential (-0.63 V vs. SCE) of CP is more negative than the reduction potential of O_2 to O_2^- (-0.55 V vs. SCE), offering feasibility for the production of superoxide species and enhancing the photodegradation of dyes.⁸ Conversely, the more positive VB position of P5Tz-CP makes it suitable for the oxidation of H₂O to generate ROS, as confirmed by the higher VB potential (1.73 V vs. SCE) than the oxidation potential of H₂O to H₂O₂ (1.54 V vs. SCE). And •OH could be produced from H₂O₂ as secondary ROS. Therefore, P5Tz-CP incorporated with pillararenes possesses a stronger oxidation ability, which is consistent with the scavenger effects. The photocatalytic effects are exerted by the resultant ROS that converts dyes to their corresponding degradation products. Then, the photostability was assessed by recycle experiments of P5Tz-CP and CP, respectively. Negligible deactivation after three cycles indicates excellent recyclability and stability of both P5Tz-CP and CP upon visible light illumination for a long time.

In conclusion, we constructed two conjugated polymers, P5Tz-CP and CP, bearing heteroatom-codoped TzTz units connected by alternating terphenyl units with or without pillararene rings, which displayed effective photocatalytic activity in the degradation of organic dyes in solution. Tuneable band gaps and appreciable optoelectronic properties of P5Tz-CP were discussed. The photocatalytic propensity is essentially associated with multiple factors such as contact area, particle morphology, energy band structure, and efficient charge diffusion. Broadening the tailorable building blocks is still the kernel in pursuing unprecedented properties and functions of advanced materials. This work signifies the promising future of functional macrocycles in the application of advanced polymer materials.

We acknowledge the financial support from the National Natural Science Foundation of China (21871108).

Conflicts of interest

There is no conflict to declare.

Notes and references

- 1 H. Wang, H. Wang, Z. Wang, L. Tang, G. Zeng, P. Xu, M. Chen, T. Xiong, C. Zhou, X. Li, D. Huang, Y. Zhu, Z. Wang and J. Tang, *Chem. Soc. Rev.*, 2020, **49**, 4135.
- 2 Y. Nosaka and A. Y. Nosaka, Chem. Rev., 2017, 117, 11302.
- 3 A. Iwase, S. Yoshino, T. Takayama, Y. H. Ng, R. Amal and A. Kudo, J. Am. Chem. Soc., 2016, **138**, 10260.
- 4 X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu and M. Antonietti, *J. Am. Chem. Soc.*, 2009, **131**, 1680.
- 5 D. Jiang, P. Xu, H. Wang, G. Zeng, D. Huang, M. Chen, C. Lai, C. Zhang, J. Wan and W. Xue, *Coord. Chem. Rev.*, 2018, **376**, 449.
- 6 W. Li, X. Huang, T. Zeng, Y. A. Liu, W. Hu, H. Yang, Y. B. Zhang and K. Wen, *Angew. Chem., Int. Ed.*, 2021, **60**, 1869.
- 7 X. Wang, G. Sun, P. Routh, D. H. Kim, W. Huang and P. Chen, *Chem. Soc. Rev.*, 2014, 43, 7067.
- W. Huang, N. Huber, S. Jiang, K. Landfester and K. A. I. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 18368; J. J. Lee, W. Noh, T.-H. Huh, Y.-J. Kwark and T. S. Lee, *Polymer*, 2020, **211**, 123060; Q. Yang, M. Luo, K. Liu, H. Cao and H. Yan, *Appl. Catal.*, *B*, 2020, **276**, 119174; J. Chakraborty, I. Nath, C. Jabbour, N. Aljammal, S. Song, C. M. Kao, P. M. Heynderickx and F. Verpoort, *J. Hazard. Mater.*, 2020, **398**, 122928.
- 9 Z. Li and Y. W. Yang, J. Mater. Chem. B, 2017, 5, 9278; T. Zhang, G. Xing, W. Chen and L. Chen, Mater. Chem. Front., 2020, 4, 332.
- 10 G. W. Gokel, W. M. Leevy and M. E. Weber, *Chem. Rev.*, 2004, 104, 2723.
- 11 B. V. K. J. Schmidt and C. Barner-Kowollik, Angew. Chem., Int. Ed., 2017, 56, 8350.
- 12 A. Ikeda and S. Shinkai, Chem. Rev., 1997, 97, 1713.
- 13 L. Isaacs, Acc. Chem. Res., 2014, 47, 2052.
- 14 T. Ogoshi, T.-A. Yamagishi and Y. Nakamoto, *Chem. Rev.*, 2016, **116**, 7937.
- 15 M. Wang, Q. Li, E. Li, J. Liu, J. Zhou and F. Huang, Angew. Chem., Int. Ed., 2021, 60, 8115; Z. Li and Y. W. Yang, Acc. Mater. Res., 2021, 2, 292.
- K. Jie, Y. Zhou, E. Li and F. Huang, Acc. Chem. Res., 2018, 51, 2064;
 J. R. Wu, B. Li and Y. W. Yang, Angew. Chem., Int. Ed., 2020, 59, 2251;
 J. R. Wu and Y. W. Yang, Angew. Chem., Int. Ed., 2021, 60, 1690.
- A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling and W. R. Dichtel, *Nature*, 2016, **529**, 190; D. Shetty, I. Jahovic, J. Raya, Z. Asfari, J. C. Olsen and A. Trabolsi, *ACS Appl. Mater. Interfaces*, 2018, **10**, 2976; S. N. Talapaneni, D. Kim, G. Barin, O. Buyukcakir, S. H. Je and A. Coskun, *Chem. Mater.*, 2016, **28**, 4460; X. Li, Z. Li and Y. W. Yang, *Adv. Mater.*, 2018, **30**, 1800177; Z. Li, X. Li and Y. W. Yang, *Small*, 2019, **15**, 1805509; D. Dai, J. Yang, Y. C. Zou, J. R. Wu, L. L. Tan, Y. Wang, B. Li, T. Lu, B. Wang and Y. W. Yang, *Angew. Chem., Int. Ed.*, 2021, **60**, 8967.
- 18 G. Zhang, Z.-A. Lan and X. Wang, Angew. Chem., Int. Ed., 2016, 55, 15712; Q. Huang, L. Guo, N. Wang, X. Zhu, S. Jin and B. Tan, ACS Appl. Mater. Interfaces, 2019, 11, 15861.
- 19 Q. Wang, S. Guan and B. Li, Catal. Sci. Technol., 2017, 7, 4064.