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Triphenylamine based conjugated microporous polymers for selective photoreduction of CO₂ into CO under visible light

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Abstract: Organic π -conjugated polymers (CPs) have emerged as a new platform for a variety of critical photocatalytic applications in the past few years. Nevertheless, CPs for efficient CO₂ photoreduction have been rarely reported yet, which is mainly challenged by the lack of suitable polymers with sufficient solar light harvesting ability, appropriate energy levels as well as robust activity and selectivity in multi-electron involving CO₂ photoreduction reaction. This work reports the rational design and synthesis of two novel triphenylamine (TPA) based conjugated microporous polymers (CMPs), which can efficiently reduce CO₂ to CO with water vapour without additional cocatalysts under ambient conditions. A significantly enhanced CO evolution rate of OXD-TPA (37.15 $\mu\text{mol h}^{-1} \text{g}^{-1}$) compared to BP-TPA (0.9 $\mu\text{mol h}^{-1} \text{g}^{-1}$) was achieved by the replacement of biphenyl with 2,5-diphenyl-1,3,4-oxadiazole (> 420 nm), which could be mainly ascribed to the synergistic effect of the decreased optical band gap, improved interface charge transfer, and increased CO₂ uptake. This contribution is expected to spur further interest in rational design of porous conjugated polymers for CO₂ photoreduction.

For the past few decades, artificial photocatalysis has been intensively studied as a sustainable technology to directly converse CO₂ into value-added chemicals such as CO, CH₄, CH₃OH, etc.^[1-6] The technology is particularly appealing as it not only holds great promise to handle the climate change issue caused by excess CO₂ release, but also produce valuable chemical fuels for energy supply. However, high energy input is required for CO₂ transformation owing to its remarkable stability with dissociation energy of C=O bond up to 750 kJ mol⁻¹,^[6] which makes it difficult to develop efficient photocatalysts. Since the pioneering report of the heterogeneous CO₂ photoreduction using TiO₂ as the catalysts,^[7] numerous inorganic semiconductors are under active exploration. However, they suffer from limited tunability, potential heavy-metal toxicity and wide band gap,^[7-10] which hinders their practical applications and thus require the exploitation of alternatives.

Conjugated microporous polymers (CMPs), as a kind of structurally diverse materials, show many advantages, such as permanent porosity, large surface area, strong visible light activity, facile synthesis, tunable optoelectronic properties, as well as high chemical and thermal stability, making them attractive candidates for a wide range of applications, such as gas storage and separation,^[11-15] heterogeneous catalysis,^[16-20] sensing,^[21,22] as well as energy storage and conversion.^[23-27] Recent studies have revealed that porous conjugated polymers (CPs) are promising photocatalysts for CO₂ reduction and their photocatalytic activities could be significantly improved by rational molecular design. For example, Liu and co-workers reported photocatalytic CO₂ reduction using a series of pyrene-based porous CPs in the CO₂-saturated ionic liquid, which yielded a high CO evolution rate of 47.37 $\mu\text{mol h}^{-1} \text{g}^{-1}$ with a selectivity up to 98.3% (> 420 nm).^[28] In order to reduce CO₂ under visible light, Wang et al. designed three triazine-based CPs by introducing comonomers with different electron-withdrawing/donating properties in the polymer backbone.^[29] A CO evolution rate of 18.2 $\mu\text{mol h}^{-1}$ with 81.6% selectivity was achieved in the presence of cocatalysts (CoCl₂ and dipyriddy). In addition, crystalline covalent organic framework (COF) based CO₂-reduction photocatalysts were reported by Huang et al, in which Re(bpy)(CO)₃Cl was incorporated into the 2D COF to drive CO₂ photoreduction with 98% selectivity.^[30] Despite of good activities were achieved by these conjugated polymers, organic sacrificial agents, additional cocatalysts or expensive ionic liquid were required in the photocatalytic system, which is not economical and environment-friendly enough. By contrast, directly use of H₂O as an electron donor for efficient CO₂ photoreduction would be ideal.

In this study, we presented the first example of novel CMPs as visible-light-active photocatalysts for CO₂ reduction into CO only in the presence of water vapour at ambient condition, the chemical structures of the two polymers are shown in Scheme 1. Triphenylamine (TPA) based CMPs were developed owing to their inherent advantages such as high surface area for effective CO₂ absorption, facile preparation, finely optimization of energy levels.^[31,32] The optical band gaps of as-prepared CMPs could

be tuned from 2.38 to 2.22 eV by the replacement of biphenyl (BP) with 2,5-diphenyl-1,3,4-oxadiazole (OXD). More importantly, the CO evolution rate could be enhanced to $37.15 \mu\text{mol h}^{-1} \text{g}^{-1}$ under visible light irradiation ($> 420 \text{ nm}$). In addition, we explored systematically an integrated experimental and computational study to provide a proper understanding of the structure-property relationship of the two polymers, which is critical for future development of conjugated polymers for CO_2 photoreduction. The synthetic details and characterization of the monomers and polymers are shown in the Supporting Information. Tris(4-ethynylphenyl)amine was prepared by coupling tris(4-bromophenyl)amine with ethynyltrimethylsilane using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$ as catalyst and the subsequent deprotection promoted by K_2CO_3 .^[33] 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole was synthesized from 4-bromobenzoyl chloride in three steps as

Scheme 1. Chemical structures of the conjugated microporous polymers for CO_2 photoreduction in this study.

shown in Scheme S1. Condensation reaction between 4-bromobenzoyl chloride and hydrazine hydrate to afford 1,2-bis(4-bromobenzoyl)hydrazide, which was further converted to 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole in high yield by cyclodehydration using POCl_3 .^[34] BP-TPA and OXD-TPA were synthesized from tris(4-ethynylphenyl)amine with 4,4'-dibromodiphenyl and 2,5-diphenyl-1,3,4-oxadiazole, respectively, by Sonogashira coupling reaction in DMF/ Et_3N (1:1, v/v) mixture with $\text{Pd}(\text{PPh}_3)_4$ and CuI as catalysts. The crude product was successively washed with methanol, water and acetone following by Soxhlet extraction (THF and then CH_2Cl_2) and collected above 90% yield. BP-TPA and OXD-TPA are insoluble in organic solvents such as DMF, CH_2Cl_2 and THF. The detailed chemical structures of the two polymers were characterized by solid-state ^{13}C NMR spectroscopy, FT-IR spectra, and elemental analysis. Both of the two polymers show aromatic peaks at 120-150 ppm and peaks at ~ 91 ppm for quaternary alkynes (Figure S1-S2), consistent with CMPs synthesized by Sonogashira polymerization.^[33] In addition, the peak at 163 ppm in NMR spectrum of OXD-TPA is ascribed to the carbon atom of oxadiazole. Fourier-transform infrared (FT-IR) spectra analysis confirmed the alkynyl linkage of the two polymers by the evidence of stretching vibrations of triple bonds appearing around 2200 cm^{-1} (Figure S3). BP-TPA and OXD-TPA show similarly spherical morphologies revealed by scanning electron microscopy (SEM) measurement (Figure S4). The residual Pd content in the polymer networks is negligibly low at 0.34% for BP-TPA and 0.54% for OXD-TPA, respectively. The powder X-ray diffraction (PXRD) patterns revealed that both of the two polymers exhibited broad diffraction peaks with low intensities in the wide region, indicating they are amorphous in nature (Figure S6). Thermal gravimetric analysis (TGA) demonstrated their excellent stability with 5% weight loss of for BP-TPA and OXD-TPA were observed at 463°C and 412°C , respectively (Figure S7).

The porosity of BP-TPA and OXD-TPA was evaluated by the N_2 sorption isotherm measurements at 77 K. As shown in Figure 1a, both of the two networks gave rise to type I nitrogen gas sorption isotherms and exhibited a steep increase in the low relative pressure regions (< 0.01) due to their microporosity. The apparent BET surface area of BP-TPA is $512 \text{ m}^2 \text{ g}^{-1}$, which is lower than that of OXD-TPA ($686 \text{ m}^2 \text{ g}^{-1}$). The analysis by nonlocal density functional theory (NL-DFT) show both of the two polymers have similar pore size distributions and their pore widths centering at about 1.1, 1.5 and 2.7 nm, respectively (Figure S5). This reflects a considerable proportion of micropores existing in the two networks. The CO_2 uptake capacities of the two polymers at 298 K were evaluated by CO_2 adsorption isotherms. OXD-TPA incorporated 1,3,4-oxadiazole exhibited a higher volumetric CO_2 uptake than BP-TPA (Figure 1b). In particular, the difference of CO_2 uptake became more distinct with increasing pressure. At $P = 100 \text{ kPa}$, the CO_2 uptake capacities of BP-TPA and OXD-TPA were 24.1 and $30.3 \text{ cm}^3 \text{ g}^{-1}$, respectively. The enhanced CO_2 absorbing ability of OXD-TPA compared to BP-TPA is likely attributed to its higher BET surface area and the dipole-induced electrostatic interactions between the carbon atoms of CO_2 and the N or O atoms of oxadiazole unit, which was revealed by many reports.^[35-37]

Figure 1. (a) N₂ sorption isotherm curves of the polymers measured at 77 K. (b) CO₂ adsorption isotherm curves of the polymers at 298 K.

The UV/vis diffuse reflectance spectra (DRS) and solid-state fluorescence spectra of BP-TPA and OXD-TPA are shown in Figure 2a. OXD-TPA with extended π -conjugation shows broader adsorption compared with that of BP-TPA. Accordingly, the optical bandgaps estimated from absorption onset of the DRS spectra are 2.38 eV for BP-TPA and 2.22 eV for OXD-TPA. Upon excitation of 380 nm, BP-TPA exhibits a weak fluorescence centered at 562 nm, which is slightly red-shifted to 557 nm for OXD-TPA. Notably, the photoluminescence (PL) emission of OXD-TPA is significantly stronger than that of BP-TPA. It is probably that the twisted conformation between phenyl and oxadiazole in 2,5-diphenyl-1,3,4-oxadiazole will interrupt the π -conjugation and molecular stacking of conjugated unit, thus probably blue-shift the emission and enhance the fluorescence intensity.^[38,39] In addition, the time-resolved PL decay spectra demonstrated a slightly longer excited state fluorescence lifetime of 0.82 ns for OXD-TPA than BP-TPA (0.61 ns) (Figure S8). The LUMO levels of the two polymers were evaluated using cyclic voltammetry (Figure S9). Both of them exhibited well-defined reversible reduction waves with the LUMO levels of -0.41 V (vs. NHE) for BP-TPA and -0.44 V (vs. NHE) for OXD-TPA (Table 1). Accordingly, the HOMO levels of BP-TPA and OXD-TPA were calculated to be 1.97 V and 1.78 V, respectively. The energy band structures of both polymers are well positioned for the reduction of CO₂ to CO and CH₄, indicating that they are thermodynamically capable of CO₂ photoreduction to generate corresponding gaseous products under light irradiation.^[40]

Figure 2. (a) UV/vis DRS (solid line) and photoluminescence (PL) spectra (dashed lines; $\lambda_{\text{ex}} = 380$ nm) of BP-TPA and OXD-TPA in the solid state. (b) Energy levels of BP-TPA and OXD-TPA relative to the potentials of CO₂ reduction to CO and CH₄, as well as water reduction and oxidation, respectively, vs the NHE at pH = 0. (c) EIS Nyquist plots and (d) periodic transient photocurrents response of polymers electrodes in 0.5 M Na₂SO₄ aqueous solution.

Table 1. Optical and electrochemical properties, BET surface area and CO₂ uptake data of the polymers.

Polymer	E _g ^[a] (eV)	E _{red,onset} (V) ^[b]	LUMO/HOMO (V, vs. NHE) ^[c]	S _{BET} (m ² g ⁻¹)	CO ₂ uptake ^[d] (cm ³ g ⁻¹)
BP-TPA	2.38	-1.04	-0.41/1.97	512	24.1
OXD-TPA	2.22	-1.07	-0.44/1.78	686	30.3

[a] Estimated from DRS absorption onset ($E_g^{opt} = 1240/\lambda_{onset}$). [b] Versus Fc/Fc⁺ in acetonitrile solution, 50 mV s⁻¹ scan rate. [c] $E_{NHE} = E_{Fc/Fc^+} + 0.63$ V; $E_{HOMO} = E_{LUMO} - E_{g,opt}$; [d] P/P₀ = 1, measured at 1 bar.

Electrochemical impedance spectroscopy (EIS) and the transient photocurrent response were measured to compare photogenerated charge carriers transport of the two polymers. As displayed in Figure 2c, the Nyquist plot of OXD-TPA exhibits a smaller diameter of the semicircular than that of BP-TPA, revealing that decrease of the charge-transfer resistance by the replacement of biphenyl using 2,5-diphenyl-1,3,4-oxadiazole. The improved photoinduced charge transport can be further supported by increased transit photocurrent response of OXD-TPA as shown in Figure 2d, which shows a visible-light photocurrent of ~ 2 µA/cm² for OXD-TPA and ~ 0.5 µA/cm² for BP-TPA.

The CO₂ photoreduction reactions over the as-synthesized polymers were carried out in the presence of CO₂ and water vapour under ambient conditions. As shown in Figure 3a, after the four-hour irradiation of visible light (> 420 nm), OXD-TPA produced 148.6 µmol g⁻¹ CO, which is much more than BP-TPA (3.6 µmol g⁻¹). To the best of our knowledge, the photocatalytic activity of OXD-TPA (37.15 µmol h⁻¹ g⁻¹) is super good as compared to that of commonly used g-C₃N₄ and many newly reported g-C₃N₄ composites under the similar conditions (Table S1).

In order to confirm the photocatalytic process, we have performed a series of control experiments. No any reductive products were detected under dark conditions. While replacing CO₂ with N₂, only trace CO could be detected, indicating CO₂ is served as reductive agent in the system. In the case of no H₂O added in the reaction system, negligible CO could be measured, which indicates that H₂O plays an important role as an electron donor. Other products, such as CH₄, H₂, HCOOH, HCHO, CH₃OH, were not detected probably because of the gas-phase CO₂ photoreduction with low proton concentrations in our photocatalytic system.

To figure out that the source of evolved CO during the photocatalytic process, isotopic experiment with ¹³CO₂ were undertaken under same reaction condition (> 420 nm). As shown in Figure S12, mass spectrum signals of ¹³CO (*m/z* = 29) were clearly observed during the photocatalytic reaction, indicating that CO are originated from the CO₂ reduction on OXD-TPA.

The photocatalytic CO₂ reduction stability and recyclability of OXD-TPA was evaluated by four cyclic testing (4h-irradiation in each run). The reactor was vacuum and refilled the mixture of CO₂ and water vapour after each run. It can be seen that steady gas evolution is observed over four runs irradiation (Figure 3b). After the photocatalysis experiments, the recycled polymer did not show any significant structural changes (Figure S13-S15), indicating the OXD-TPA is highly stable during the whole photocatalytic process.

Figure 3. (a) CO evolution from the photocatalytic CO_2 reduction on BP-TPA and OXD-TPA after 4-h irradiation (> 420 nm). Reaction conditions: 15 mg polymer, CO_2 (1.0 atm), water vapour, room temperature. (b) Repeated photocatalytic reduction of CO_2 over OXD-TPA (> 420 nm).

DFT calculations were performed to understand their electronic properties of the two CMPs and the optimized structures are shown in Figure S16. As displayed in Figure 4a and 4b, the excited electrons for both BP-TPA and OXD-TPA are distributed all over the backbone, whereas the excited holes are mainly localized in the TPA region due to its strong electron-donating feature. Moreover, compared to BP moiety, the more electronegative OXD moiety impairs the density of excited electrons within the TPA part, which lead to the overlap between excited electrons and holes in OXD-TPA is much less than in BP-TPA, indicating less recombination of photogenerated excitons in OXD-TPA.

We further studied the adsorption energy of COOH^* , which is proposed to be the intermediate for CO_2 reduction to CO, on different positions of BP-TPA and OXD-TPA (Figure S17), and the most stable COOH^* are shown in Figure 4c. The adsorbed COOH^* has similar configurations but the adsorption is ~ 0.2 eV more stable on OXD-TPA, which facilitates the reduction of CO_2 .

Hybrid DFT calculations revealed that the band gaps for BP-TPA and OXD-TPA are 2.47 and 2.38 eV, respectively, which are in reasonable agreement with the optical bandgaps obtained in our experiments (2.38 eV for BP-TPA and 2.22 eV for OXD-TPA as shown in Table 1). Notably, the theoretically predicted HOMOs and LUMOs for BP-TPA and OXD-TPA are depicted in Figure S18. The HOMO potential of BP-TPA (0.79 V) is approximate to the one required for water oxidation (0.82 V), while it is 0.27 V more positive for OXD-TPA. The LUMO potentials of both BP-TPA (-1.68 V) and OXD-TPA (-1.31 V) are much more negative than the reduction potential of CO_2 to CO (-0.53 V). The results confirmed

Figure 4. (a) Excited-state hole distribution (0.001 e/bohr^3), (b) excited-state electron distribution (0.001 e/bohr^3), and (c) optimized intermediate COOH^* for BP-TPA and OXD-TPA.

the redox ability of the two polymers, which is critical for them to trigger the photocatalytic reactions in our system. The much better performance of OXD-TPA comes from its smaller band gap, increased dissociation of photogenerated excitons, and more stable COOH*.

In conclusion, for the first time, we present the rational design of two novel triphenylamine based CMPs for CO₂ photoreduction into CO under visible light irradiation. The CO evolution rate could be significantly enhanced from 0.9 to 37.15 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (> 420 nm). The enhancement in photocatalytic activity by molecular tuning was fully investigated by the experiment and theoretical calculation. Accordingly, we expect that this contribution can pave the way to design stable and highly efficient conjugated polymers for CO₂ photoreduction.

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Keywords: visible light • CO₂ reduction • triphenylamine • conjugated microporous polymers

- [1] J. L. White, M. F. Baruch, J. E. Pander, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* **2015**, *115*, 12888.
- [2] M. Marszewski, S. Cao, J. Yu, M. Jaroniec, *Mater. Horiz.* **2015**, *2*, 261.
- [3] K. Li, B. Peng, T. Peng, *ACS Catal.* **2016**, *6*, 7485.
- [4] R. Shi, G. I. N. Waterhouse, T. Zhang, *Sol. RRL* **2017**, *1*, 1700126.
- [5] J. Ran, M. Jaroniec, S.-Z. Qiao, *Adv. Mater.* **2018**, *30*, 1704649.
- [6] Z. Sun, N. Talreja, H. Tao, J. Texter, M. Muhler, J. Strunk, J. Chen, *Angew. Chem. Int. Ed.* **2018**, *57*, 7610.
- [7] T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **1979**, *277*, 637.
- [8] A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, *Energy Environ. Sci.* **2012**, *5*, 9217.
- [9] S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.* **2013**, *52*, 7372.
- [10] K. Li, B. Peng, T. Peng, *ACS Catal.* **2016**, *6*, 7485.
- [11] A. Li, R. F. Lu, Y. Wang, X. Wang, K. L. Han, W. Q. Deng, *Angew. Chem. Int. Ed.* **2010**, *49*, 3330.
- [12] R. Dawson, E. Stockel, J. R. Holst, D. J. Adams, A. I. Cooper, *Energy Environ. Sci.* **2011**, *4*, 4239.
- [13] Q. Chen, M. Luo, P. Hammershøj, D. Zhou, Y. Han, B. W. Laursen, C.-G. Yan, B.-H. Han, *J. Am. Chem. Soc.* **2012**, *134*, 6084.
- [14] Y. H. Xu, S. B. Jin, H. Xu, A. Nagai, D. L. Jiang, *Chem. Soc. Rev.* **2013**, *42*, 8012.
- [15] Y. Yuan, H. Huang, L. Chen, Y. Chen, *Macromolecules* **2017**, *50*, 4993.
- [16] L. Chen, Y. Yang, Z. Guo, D. Jiang, *Adv. Mater.* **2011**, *23*, 3149.
- [17] K. Zhang, D. Kopetzki, P. H. Seeberger, M. Antonietti, F. Vilela, *Angew. Chem. Int. Ed.* **2013**, *52*, 1432.
- [18] Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Adv. Mater.* **2015**, *27*, 6265.
- [19] Y.-B. Zhou, Y.-Q. Wang, L.-C. Ning, Z.-C. Ding, W.-L. Wang, C.-K. Ding, R.-H. Li, J.-J. Chen, X. Lu, Y.-J. Ding, Z.-P. Zhan, *J. Am. Chem. Soc.* **2017**, *139*, 3966.
- [20] R. Li, J. Byun, W. Huang, C. Ayed, L. Wang, K. A. I. Zhang, *ACS Catal.* **2018**, *8*, 4735.
- [21] X. Liu, Y. Xu, D. Jiang, *J. Am. Chem. Soc.* **2012**, *134*, 8738.
- [22] C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu, D. Jiang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4850.
- [23] Y. Kou, Y. Xu, Z. Guo, D. Jiang, *Angew. Chem. Int. Ed.* **2011**, *50*, 8753.
- [24] F. Vilela, K. Zhang, M. Antonietti, *Energy Environ. Sci.* **2012**, *5*, 7819.
- [25] C. Gu, N. Huang, Y. Chen, L. Qin, H. Xu, S. Zhang, F. Li, Y. Ma, D. Jiang, *Angew. Chem. Int. Ed.* **2015**, *54*, 13594.
- [26] C. Zhang, Y. He, P. Mu, X. Wang, Q. He, Y. Chen, J. Zeng, F. Wang, Y. Xu, J.-X. Jiang, *Adv. Funct. Mater.* **2018**, *28*, 1705432.
- [27] J. Zhu, C. Yang, C. Lu, F. Zhang, Z. Yuan, *Acc. Chem. Res.* **2018**, *51*, 3191.
- [28] Y. Chen, G. Ji, S. Guo, B. Yu, Y. Zhao, Y. Wu, H. Zhang, Z. Liu, B. Han, Z. Liu, *Green Chem.* **2017**, *19*, 5777.
- [29] C. Yang, W. Huang, L. C. da Silva, K. A. I. Zhang, X. Wang, *Chem. Eur. J.* **2018**, *24*, 17454.
- [30] S. Yang, W. Hu, X. Zhang, P. He, B. Pattengale, C. Liu, M. Cendejas, I. Hermans, X. Zhang, J. Zhang, J. Huang, *J. Am. Chem. Soc.* **2018**, *140*, 14614.
- [31] T. Geng, Z. Zhu, W. Zhang, Y. Wang, *J. Mater. Chem. A* **2017**, *5*, 7612.
- [32] Z. Chen, W. Li, Y. Dai, N. Xu, C. Su, J. Liu, C. Zhang, *Electrochim. Acta* **2018**, *286*, 187.
- [33] Z. Xie, Y. Wei, X. Zhao, Y. Li, S. Ding, L. Chen, *Mater. Chem. Front.* **2017**, *1*, 867.
- [34] W.-Y. Wong, Y.-H. Guo, *J. Mol. Struct.* **2008**, *890*, 150.
- [35] M. Saleh, H. M. Lee, K. C. Kemp, K. S. Kim, *ACS Appl. Mater. Interfaces* **2014**, *6*, 7325.
- [36] S. Hug, L. Stegbauer, H. Oh, M. Hirscher, B. V. Lotsch, *Chem. Mater.* **2015**, *27*, 8001.
- [37] K. Yuan, C. Liu, L. Zong, G. Yu, S. Cheng, J. Wang, Z. Weng, X. Jian, *ACS Appl. Mater. Interfaces* **2017**, *9*, 13201.

- [38] C. Wang, L.-O. Pålsson, A. S. Batsanov, M. R. Bryce, *J. Am. Chem. Soc.* **2006**, 128, 3789.
- [39] Y. Tao, Q. Wang, C. Yang, C. Zhong, K. Zhang, J. Qin, D. Ma, *Adv. Funct. Mater.* **2010**, 20, 304.
- [40] W. Fan, Q. Zhang, Y. Wang, *Phys. Chem. Chem. Phys.* **2013**, 15, 2632.