BODIPY-Based Porous Organic Polymers: How the Monomeric Methyl Substituents and Isomerization Affect the Porosity and Singlet Oxygen Generation

De-Gao Wang, Qian Li, Yunlong Zhu, Hui Tang, Min Song,* Gui-Chao Kuang*

Facile Friedel–Crafts coupling reaction prepared porous organic polymers BDP-POP-n (n = 1, 3, and 4) are reported. The influences of methyl substituents and single monomer isomerization on corresponding BDP-POPs’s porosity and singlet oxygen generation properties have been investigated. The obtained BDP-POPs are thoroughly characterized by a combination of techniques such as Fourier transform infrared, solid 13C NMR, scanning electron microscopy, and transmission electron microscopy. In addition, these porous polymers’ singlet oxygen generation capacities under visible green light (480–510 nm) irradiation are compared. Results show that BDP-POP-1, whose pyrrolyl ring bears methyl substituents and the two 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BDP) units are at para-position of the phenyl ring, possesses the largest Brunauer–Emmett–Teller surface area and the best singlet oxygen generation ability. Control experiment reveals that the BDP-POP-1 shows superiority in generating singlet oxygen than that of model polymer CMPBDP. It is believed that this work may pave a road to design more effective porous materials for photocatalysis.

1. Introduction

In recent years, porous organic polymers (POPs) have shown promising applications in various fields such as photocatalysis,1–3 solar cell,4,5 CO2 capture,6–8 hydrogen storage,9 and so on for their advantages in the intrinsic porosity, thermal stability, narrow pore distribution, and low density. Various conjugated POPs have been developed by carbon–carbon cross-coupling reactions such as Suzuki coupling reaction, Sonogashira coupling reaction, and Yamamoto coupling reaction.10 However, these coupling reactions are suffering the limitation of expensive metal catalysts and high reaction temperature. In addition, normally two different monomers with functional groups are preferred to do cross-coupling reaction.11 Therefore, facile preparation of conjugated POPs with a single monomer by using cheap catalyst might show superiority at a certain extent.12–14

Singlet oxygen (1O2) has shown its fascinating perspectives in photodynamic therapy,15 organic synthesis,16 and so forth. Among all the POPs provided
with $^{1}$O$_2$ generation capacities, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (or BDP)-based POPs have drawn researchers’ attention in recent years for the BODIPY units showing low luminescent property, stability, and photoactivity. Liras et al. prepared BODIPY-based porous polymer (CMPBDP) as a photocatalyst for the oxidation of thioanisole.[16] Afterward, in the same lab, they developed BODIPY-based conjugated polymer as an efficient photocatalyst for minimum ion generation.[17] Vilela and co-workers demonstrated a BODIPY-based POPs as reusable heterogeneous photosensitizer in a photochemical flow reactor.[18] The ability of POPs for the production of $^{1}$O$_2$ was monitored by $^1$H NMR during the oxidation process. In addition, Jiang and co-workers prepared a series of BODIPY-based POPs and investigated their CO$_2$ adsorption properties.[19] Although progresses have been made in this field, these POPs are prepared using traditional cross-coupling reaction with expensive catalysts and at least two different monomers with functional group are needed.

Inspired by the work of Bard and co-workers that the 2,6-position of BODIPY units are reactive and could be oxidized by FeCl$_3$ at ambient temperature, therefore, we initiated a research program to address the above problems by using BODIPY-based monomers. We made three dimeric BODIPY monomers with different spacers and got corresponding POPs by facile Friedel–Crafts coupling reactions with cheap FeCl$_3$ catalyst. It was found that the porosity and photophysical properties are dependent on the linkage between the dimeric BODIPY units. On the basis of our understanding of monomeric structures showing profound effect on the POPs properties, herein, we have enabled some advances in designing new dimeric BODIPY monomers without methyl substituents or the monomers with isomeric architectures. Facile oxidations of these new monomers by FeCl$_3$ were proceeded to obtain corresponding POPs. We hope to set up some fundamental parameters for designing the BODIPY-based POPs by various structural variations such as spacer, substitution, and isomerization.

2. Experimental Section

2.1. Materials

All chemical reagents were commercially available and used as received unless otherwise stated. Dichloromethane (DCM) was dried by standard methods using CaCl$_2$ before distillation using distilling apparatus. All reactions were performed under an inert atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed using TLC plates precoated with silica gel (TLC: 10–40 µm, 0.2 ± 0.03 mm). Flash column chromatography was performed using 40–63 µm (230–400 mesh) silica gels as the stationary phase.

2.2. Structure Characterization and Synthesis

The $^1$H and solid $^{13}$C NMR spectra were obtained from a Bruker Avance spectrometer at 500 and 125 MHz, respectively. All chemical shifts were reported in $\delta$ units relative to tetramethylsilane. A Hitachi U-5100 was used to measure UV–vis absorption spectra. A Hitachi F-2700 was used to perform fluorescence measurements. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 and reported in terms of the frequency of absorption (cm$^{-1}$). Samples were prepared by dispersing in anhydrous KBr. Solid-state cross-polarization magic angle spinning ($^{13}$C ($^1$H)) NMR spectra were recorded from an AVANCE $\| 500$ MHz produced by Bruker. Thermogravimetric analyses were conducted in an N$_2$ stream with an STD Q600 V8.0 Build 95 analyzer. The samples were heated from room temperature (rt) to 800 °C with a heating rate of 10 °C min$^{-1}$ under N$_2$ atmosphere. Scanning electron microscopy (SEM) images and Energy-dispersive spectroscopy (EDS) measurements of BDP-POPs were made in a FEI SIRION200 microscope with an accelerating voltage of 10 and 20 kV, respectively. All the samples were coated with gold before test. High-resolution transmission electron microscopy (TEM) images of BDP-POPs were performed on a JEOLEM-2100F microscope with an accelerating voltage of 200 kV. Prior to TEM measurements, samples were ultrasonically dispersed in ethanol and dropped to a copper grid with a diameter of 3 mm and coated with carbon film. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 sorption analyzer. According to the absorption–desorption isotherms, Brunauer–Emmett–Teller (BET) specific surface area, pore size distribution and pore volume could be evaluated. Before each measurement, the samples were degassed at 120 °C for 6 h.

The procedure for preparation of the monomers BDP-n (n = 1, 3, and 4) are similar and according to the literature.[21,22]

2.2.1. Synthesis of BDP-1

The final product BDP-1 was purified by chromatography silica gel column with an eluting solvent of petroleum ether (PE)-DCM (1:1, v/v) and afford the product BDP-1 as red power (187 mg, 21%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.52 (s, 4 H, Ar-H), 6.01 (s, 4 H, pyrrole-H), 2.57 (s, 12 H, CH$_3$), 1.52 (s, 12 H, CH$_3$).

2.2.2. Synthesis of BDP-3

The final product BDP-3 was purified by chromatography silica gel column with an eluting solvent of PE-DCM (1:5, v/v) and afford the product BDP-3 as red power (187 mg, 21%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.01 (s, 4 H, pyrrole-H), 7.76 (s, 4 H, Ar-H), 7.00 (d, 4 H, pyrrole-H), 6.60 (d, 4 H, pyrrole-H).

2.2.3. Synthesis of BDP-4

The final product BDP-4 was purified by chromatography silica gel column with an eluting solvent of PE-DCM (1:4, v/v) and afford the product BDP-4 as red power (230 mg, 15%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.99 (s, 4 H, pyrrole-H), 7.82–7.79 (m, 3 H, Ar-H), 7.75–7.71 (m, 1 H, Ar-H), 6.95 (d, 4 H, pyrrole-H), 6.59 (d, 4 H, pyrrole-H).
2.2.4. Synthesis of BDP-POPs

The preparation and treatment of BDP-POP-\(n\) \((n = 1, 3, \text{ and } 4)\) were in a similar way. A typical procedure for preparation of BDP-POP-1 was given as follows: BDP-1 (100 mg, 0.18 mmol) was dissolved in anhydrous 1,2-dichloroethane (8 mL). The mixture was degassed by three freeze–pump–thaw cycles and then FeCl\(_3\) (234 mg, 1.44 mmol) was added into the mixture under N\(_2\) atmosphere. After that, the mixture was degassed by three freeze–pump–thaw cycles and then kept at 25 °C oil bath with stirring for 48 h. The precipitate was obtained by filtration and washed by vast quantities of dichloromethane, tetrahydrofuran (THF), and chloroform. To guarantee a total removal of impurities, the precipitate was further purified by Soxhlet extraction with tetrahydrofuran, acetone, chloroform, methanol, and water for 24 h, respectively. Finally, the solid was freeze dried for 3 d to afford black powders BDP-POP-1 (70 mg, 70%). BDP-POP-3 and BDP-POP-4 were synthesized by the similar route with a yield of 75% and 65%, respectively.

2.2.5. Synthesis of Model Compound CMPBDP

The model porous polymer CMPBDP was prepared according to reported procedure.\(^{[16]}\)

3. Results and Discussion

Synthetic routes for monomer BDP-n \((n = 1, 3, \text{ and } 4)\) and corresponding polymers were described in Scheme 1. Compared to the purification of the intermediate during the synthesis of BDP-3 and BDP-4, BDP-1 was made through one-pot method. All the synthetic dimeric BODIPY monomers were verified by \(^1\)H NMR (Supporting Information). BDP-POPs were collected by filtration after a FeCl\(_3\) catalyzed Friedel–Crafts coupling reaction when the reaction proceeded 48 h. These polymers were further purified by Soxhlet extraction with chloroform, tetrahydrofuran, acetone, methanol, and water for 24 h, respectively.

The structures of BDP-POPs were characterized by FT-IR and solid \(^{13}\)C NMR. FT-IR spectra showed that the vibration peaks ascribed to the BODIPY monomers were detected in their corresponding polymers (Figure S1, Supporting Information). For example, characteristic peaks of BODIPY cores are at 1549, 1200, and 1005 cm\(^{-1}\). Peaks around 170 ppm may assign to the new-formed C–C bonds in the solid 13C NMR spectrum (Figure S2, Supporting Information). It also can be seen that the peaks around in the 128 ppm were contributed to the benzene and pyrrolyl ring. The main differences among BDP-POP-1 and other two polymers emerged in the solid 13C NMR spectrum was the peak around 128 ppm. EDS was further used to confirm the polymer element components (Figure S3, Supporting Information). After purification, little iron element signal was detected, indicating that the catalyst was effectively removed. The existence of the chlorine may be caused by the chloride covalently bonding to the polymer chain during the polymerization.\(^{[23]}\) Brown et al. pointed out that the ferric chloride can react easily with carbon radicals.\(^{[24]}\) McCarley et al. contributed the source of chlorine in the
polymers to ferric chloride.\textsuperscript{[25]} Thermal gravity analysis (TGA) curves (Figure S4, Supporting Information) suggested that the BDP-POPs were thermal stable and would not decompose until the temperature raised up to 300 °C.

The porous morphologies of all the BDP-POPs were revealed by SEM and TEM unambiguously (Figure 1). For SEM images, BDP-POP-1 displays worm-like architecture and BDP-POP-3 shows net-like structure. Both morphologies would give a gift to increase surface areas of the polymers. It is worth mentioning that BDP-POP-4 produces a solid plate feature with poor pore characteristics. TEM images were in line with the SEM results. For BDP-POP-1 and BDP-POP-3, the images show small and well-distributed pores, while BDP-POP-4 image reveals
big pores in various way. This result might suggest that the BET surface area of the previous two polymers is larger than that of BDP-POP-4.

Pore properties of the BDP-POPs were further evaluated by nitrogen gas absorption/desorption measurements at 77 K (Figure 2). According to the international union of pure and applied chemistry (IUPAC), the characteristic features of type-I isotherm is a very sharp uptake at low-pressure ratio pressure ($P/P_0 < 0.05$), which is typical for the microporous materials. The hysteresis at high pressure region suggests mesoporous architecture. Dramatic differences could be observed between BDP-POP-1 and other two polymers. BDP-POP-1 presents coexist of type-I and type-IV isotherms, which infers microporous and mesoporous architecture. In contrast, BDP-POP-3 and BDP-POP-4 presented mesoporous architecture and this can be contributed to the lack of methyl substituents as a support for the porous structures. Detailed porous properties were summarized in Table 1.

### Table 1. Porosity parameters of POPs studied in this work.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$S_{BET}$ [m$^2$ g$^{-1}$]</th>
<th>$S_{micro}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{total}$ [cm$^3$ g$^{-1}$]</th>
<th>$D_{pore}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDP-POP-1</td>
<td>358</td>
<td>254</td>
<td>0.26</td>
<td>3.0</td>
</tr>
<tr>
<td>BDP-POP-3</td>
<td>85</td>
<td>42.5</td>
<td>0.13</td>
<td>6.0</td>
</tr>
<tr>
<td>BDP-POP-4</td>
<td>39</td>
<td>11.3</td>
<td>0.08</td>
<td>8.0</td>
</tr>
</tbody>
</table>

BODIPY derivatives have been well reported for their excellent photophysical properties. In addition, they could generate $O_2$ under irradiation for some selective oxidation reactions.$^{[26,27]}$ Therefore, the fluorescence properties and the photocatalytic ability of BODIPY-based POPs for organic synthesis have been widely referred.$^{[17,18,28–30]}$ Herein, we explored the fluorescence properties of the dimeric BODIPY monomers in organic solvents and corresponding POPs at solid states. The normalized fluorescence spectra of BDP-$n$ ($n = 1, 3, and 4$) were collected in THF (Figure S5, Supporting Information). BDP-3, without methyl groups at the pyrrolyl ring, presented its emission spectrum maximum at 550 nm, which was bathochromic shifted 30 nm for that of BDP-1. BDP-4 showed its emission band peak at 530 nm. This result indicates that both methyl substituents and the BODIPY units’ isomerization have crucial effect on the electronic level of the monomers. Fluorescence microscope images of BDP-POP-$n$ ($n = 1, 3, and 4$) in solid state were taken in the same condition (Figure 1g–i). BDP-POP-1 was highly emissive, while BDP-POP-3 and BDP-POP-4 were almost not emissive.

From the point of the authors, this discrimination might come from the fluorescence differences of corresponding monomers shown in Figure S7 (Supporting Information), the BDP-1 shows the strongest fluorescence intensity and only weak intensity can be detected for other two monomers at identical measurement condition.

![Figure 3](image-url)
BODIPY-based polymers can generate \(^1\text{O}_2\) when they are exposed to visible light for their attractive photon absorption and porous structure.\(^{[16]}\) Vilela and co-workers demonstrated that surface area of POPs had profound impact on the generation of \(^1\text{O}_2\).\(^{[31]}\) We found that the methyl substituents on the pyrrolyl ring and BODIPY chromophore isomerization of the monomer would influence \(^1\text{O}_2\) generation capacities (Figure 3). In this case, we wondered whether the \(^1\text{O}_2\) generation capacities of POPs synthesized from these monomers differ or not. The generation rate of \(^1\text{O}_2\) in DMF was faster than in other solvents (Figure 4). Control experiments were performed under discriminative conditions including no light, no oxygen and no light or oxygen shown in Figure S8 (Supporting Information). In the situation of no oxygen, there still exists a decline of the concentration of the DBPF, this may be from the residual oxygen in the POPs. Irradiated with a low power green LED lamp (wavelength: 480–510 nm, 25 W; the optical source was selected according to their ultraviolet absorption, Figures S9 and S10, Supporting Information), the photocatalytic capacities of BDP-POP-\(n\) (\(n = 1, 3,\) and 4) were monitored by time-dependent electronic absorption spectroscopy. Upon irradiation, \(^1\text{O}_2\) was persistently generated which can be evidenced by the decrease of peak at 414 nm, the absorption maximum of DPBF. It should be noted that there was little difference in maximum absorption peak of DPBF compared to previous work.\(^{[32]}\) From the absorption decay curve, the \(^1\text{O}_2\) generation could be divided to three stages. In the early stage, a sharp decrease

Figure 4. The consumption of DPBF monitored by time-dependent absorption spectra in different solvents and POPs irradiated for 30 min with a low power green LED lamp. Test conditions: DPBF (4 \(\times\) 10\(^{-5}\) \text{m}) in solvents (2.5 mL) solution with 0.1 mg POPs, respectively.

Figure 5. Time-dependent absorption spectra of DPBF in dimethylformamide (DMF) upon irradiation with a low power green LED lamp: a) BDP-POP-1, b) BDP-POP-3, and c) BDP-POP-4. d) Decay kinetics of DBPF with different BDP-POPs. Test conditions: DPBF (4 \(\times\) 10\(^{-5}\) \text{m}) in DMF (2.5 mL) solution with 0.1 mg BDP-POP for (a), (b), and (c), respectively. Control experiment, a same concentration solution of DPBF was irradiated under the same condition which is shown in Figure S13 (Supporting Information). The selection of solvents was by comparison (Figure 4).
Macromolecular Chemistry and Physics

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: This work was supported by the State Key Laboratory of Powder Metallurgy, Central South University, and the Fundamental Research Funds for the Central Universities of Central South University (2015szts168).

Conflict of Interest: The authors declare no conflict of interest.

Keywords: BODIPY; methyl substituents; pore properties; porous organic polymers; singlet oxygen


4. Conclusions

In this work, we prepared three porous polymers named BDP-POP-n (n = 1, 3, and 4) through a facile FeCl₃ catalyzed Friedel–Crafts coupling reactions with moderate yields. The monomer structure variation has dramatic influence on the porous properties and singlet oxygen generation capacity. Among the three porous polymers, BDP-POP-1 with methyl substituent on the pyrrolyl ring and the two BODIPY units are at para-position shows the largest BET and best capacity to generate ¹O₂. The detailed catalytic applications for organic reaction are underway in our laboratory. From the point of the authors, this work may contribute to design and develop more effective photocatalyst.

© 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

www.advancedsciencenews.com

Figure 6. Recycle experiments of BDP-POP-1 in DMF. A diminutive decline (shown as an arrow) can be found in the third cycle. Test condition: DPBF (4 × 10⁻⁵ m) in DMF (2.5 mL) solution with 0.1 mg BDP-POP-1. When a cycle finished, the solid was filtered and added to a new DPBF (4 × 10⁻⁵ m) in DMF (2.5 mL) solution.

can be seen (irradiation at the first 5 min). In the medium stage (irradiation between 10 and 20 min), a steady decrease displayed. Finally, a slow drop was observed upon further irradiation (Figure 5). Decay kinetics curves clearly revealed a meticulous and intuitionistic comparison of ¹O₂ generation capacities for different BDP-POPs. BDP-POP-1 possesses the best ability for ¹O₂ generation while the BDP-POP-4 is the worst one. The methyl substituents might have a more profound effect than BODIPY units isomerization on the ¹O₂ generation. For BDP-POP-3 without methyl substituent on pyrrolyl ring, a sharp descend emerged in the curves, while for BDP-POP-4, only little change can be observed. The ability in generation of ¹O₂ has been compared with model POP CMPBDP. The BDP-POP-1 demonstrated its superiority than CMPBDP to generate ¹O₂ (Figures S11 and S12, Supporting Information). Finally, recycle experiments showed BDP-POP-1 with well photostability and cyclicity (Figure 6). In addition, the surface area correlated with methyl substituents and BODIPY units isomerization might be another crucial factor to influence for the ¹O₂ generation.