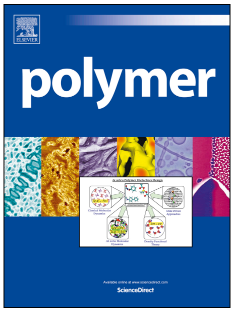

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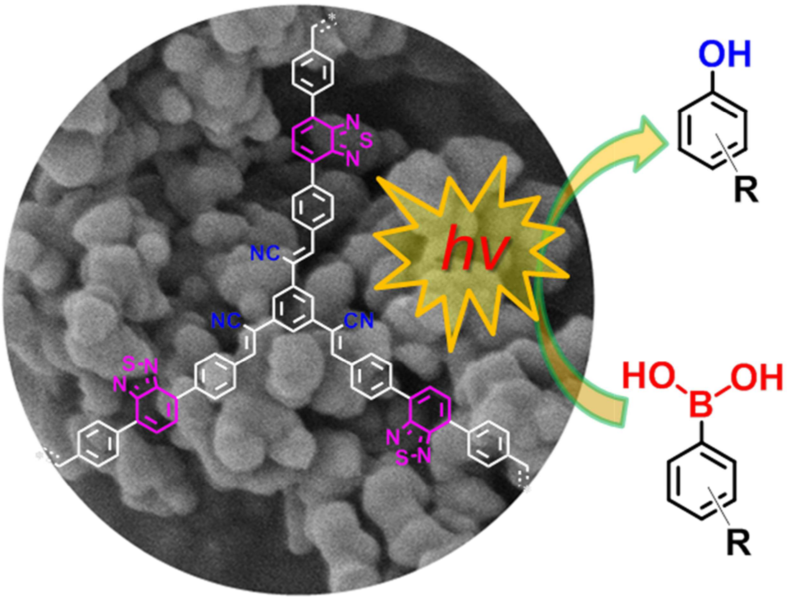
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Porous conjugated polymer via metal-free synthesis for visible light-promoted oxidative hydroxylation of arylboronic acids

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Key words:

Porous conjugated polymer, visible light, photocatalysis, oxidative hydroxylation, metal-free

Abstract

Porous conjugated polymers have emerged recently as efficient metal-free and visible light-active photocatalysts. However, the synthesis of this new class of materials usually requires transition metal catalysts such as palladium. A metal-free synthetic route still remains a huge challenge for the chemists. Here we report on a metal-free pathway of a porous conjugated polymer via simple Knoevenagel polycondensation under mild reaction conditions. The obtained polymer exhibited a high surface area and could be applied as a robust and efficient heterogeneous photocatalyst for the oxidative hydroxylation of arylboronic acids under visible light irradiation with a high functional group tolerance of the substrates.

Introduction

Sunlight is a clean and inexhaustible source of energy. As early as 1912, Ciamician first envisioned an environmentally conscious chemical industry that would replace energy-intensive synthetic processes with photochemical transformations driven by sunlight.[1] Inspired by the nature, numerous transition-metal based homogeneous photocatalysts[2-5] (e.g. Ru^{2+} or Ir^{3+} complexes) and semiconductor-based heterogeneous photocatalysts[6] (e.g. TiO_2 or Nb_2O_5) have been investigated for visible light induced organic transformations. However, due to the cost, scarcity and potential toxicity associated with these metal-based photocatalysts, the development of organic, heterogeneous, visible light-active photocatalysts has drawn surging interests for material chemists in recent years.[7-13]

Since Cooper's seminal report in 2007,[14] a variety of porous conjugated polymer (PCPs) have been developed for applications such as gas sorption,[15, 16] molecular separation,[17] green energy devices,[18] hydrogen production,[8] CO_2 conversion[19] and most recently visible light-promoted heterogeneous photocatalysis.[10, 11, 20-25] Compared to other porous counterparts such as hypercross-linked polymers (HCPs) or polymers of intrinsic microporosity (PIMs), the most characteristic feature of PCPs is the π-conjugated skeleton which leads to their outstanding light-harvesting/emitting properties, charge transfer/separation, electric energy storage properties as well as photocatalytic activities.[26]

From a synthetic perspective, an array of protocols has been reported for the preparation of porous conjugated polymers.[27, 28] Some of the most popular synthetic routes include (a) metal-mediated cross-coupling reactions (e.g. Suzuki cross-coupling,[22] Sonogashira-Hagihara-,[14, 29] Yamamoto-,[30] Glaser-,[17] Negishi-,[31] Heck-,[32] Kumada cross-coupling reactions[33] and oxidative polymerization[34]) and (b) thermally induced ring fusion reactions such as nitrile cyclization[35] and thermal polycondensation.[8] However, significant amount (e.g. 5-20 mol%) of metal catalysts (e.g. Pd, Cu, Mo, Ni, Fe) are often required for the metal mediated cross-coupling reactions.[36] Meticulous efforts have to be applied to remove the metal catalyst residuals from the resulted polymer to avoid potential interference and detrimental contamination for the intended applications. Moreover, traditional metal-free routes, such as nitrile cyclization, thermal polycondensation or phenazine ring fusion reaction, demand harsh reaction conditions (e.g. molten $ZnCl_2$ at 400 ^{0}C or calcination at 550 ^{0}C), which greatly limit the tenability of the functionalities that can be incorporated into these PCPs. Despite the widespread application and promising potentials of PCPs, there have been few reports on the metal-free synthetic pathways of PCPs under mild reaction conditions.[37, 38]

Herein, we report on a metal-free synthetic pathway of porous conjugated polymer (PCP) via simple polycondensation method under mild reaction conditions. We also demonstrate that the resulted PCP could serve as a reusable and efficient visible light heterogeneous photocatalyst for light-induced oxidative hydroxylation of arylboronic acids using molecular oxygen as green oxidant.[39, 40]

Results and discussion

The PCP was prepared using base-promoted Knoevenagel condensation of 4,7-bis(4,4'-benzaldehyde)benzo[c][1,2,5]-thiadiazole (BT-BA) and 1,3,5-benzenetriacetonitrile (BAN) in THF at 80 °C. The synthetic route of the polymer PCP-MF is displayed in Scheme 1. The experimental synthetic details and polymer characterization data are described in the ESI. The cross-linked polymer was insoluble in all common organic solvents tested. Solid state ^{13}C/MAS NMR spectroscopy showed that quaternary and tertiary aromatic carbons give rise to the broad signals between 122 ppm and 148 ppm (Figure S1 in ESI). The signals at δ = 153 ppm can be assigned to the carbon of the –C=N- groups in the benzothiadiazole units. In addition, the sp^2 carbon of double bonds in cyanostilbene unit should be at ca. 110 ppm and ca. 141 ppm which was likely molten to the main broad aromatic carbon bands. The carbon signal on cyano group appeared at 118.7 ppm.

The Brunauer-Emmett-Teller (BET) surface area of PCP-MF was found to be 130 m^2/g with a pore volume of 0.291 cm^3/g. The N_2 sorption isotherms are shown in Figure S2 in ESI. It can be noted that the polymer PCP-MF doses not only possess micropores (<2 nm), but also contains a significant amount of mesopores (2-10 nm). This could be attributed to the relatively long strut length and the rigidity of the alkenyl groups, which favor a planar configuration than 3-D networks. Thermogravimetric analysis (TGA) (Figure S4) showed that PCP-MF is thermally stable up to around 350 ^0C with less than 5% weight loss. The SEM and TEM images illustrated a fused particle-like morphology of PCP-MF (Figure 1a and 1b).The FTIR spectra of the starting compound and the polymer are displayed in Figure 1c. The signal at 1660 cm^{-1} was attributed to characteristic stretching vibration of –C=C bond in the cyanostilbene unit and signal at ca. 2360 cm^{-1} was typical for -C≡N stretching bands. The absence of stretching band at 1695 cm^{-1}, which was attributed to the carbonyl group originally from aldehydes indicated the high polymerization degree. In addition, the signals at 1348, 1377, 1567, and 1577 cm^{-1} are characteristic for the -C=N and -N−S stretching modes of benzothiadiazole unit. The FTIR spectra, consistent with solid state NMR, confirmed that photoactive benzothiadiazole moiety and cyanostilbene have been successfully combined via knoevenagel polymerization.[41]

The UV/vis DR spectrum of PCP-MF showed broad absorption of PCP-MF from the visible light to near infrared range (Figure 1d). The polymer also showed a yellowish green fluorescence with a maximum at 542 nm (Figure 1d). The electron paramagnetic resonance (EPR) displayed a remarkable increase in signal intensity under light irradiation compared to the one taken in dark, indicating the generation of long-lived photo-induced electron-hole pairs inside the polymer (Figure 1e). The results confirmed that the special structural design containing the photoactive benzothiadiazole units could enhance the light-induced charge separation and further introduce a potential redox activity of the materials.[42] The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were determined to be +1.67 V and -0.75 V *vs.* SCE via cyclic voltammetry (Figure 1f, S5 and S6). The photoredox potentials of PCP-MF are slightly lower compared to the oxidative and reductive potentials of some well-established homogeneous visible light photocatalysts, for example the $Ru(bpy)_3^+/Ru(bpy)_3^{2+}$ couple with -0.86 V and 1.29 V, respectively.[2, 4]

The photocatalytic oxidative hydroxylation of phenylboronic acid was chosen as the model reaction using PCP-MF as the photocatalyst under visible light irradiation. The reaction occurred to give the desired phenol as product in 94% yield after 10 hours (entry 1 in Table 1). Encouraged by the result, we then conducted a series of screening and control experiments as listed in Table 1. It was found that little or only trace conversion was observed if any one of the reaction components was absent, indicating that the photocatalyst PCP-MF, amine, oxygen and light are all indispensable components for this reaction (entries 2-4).

Previous studies reported that the two active oxygen species, superoxide ($O_2^{\bullet-}$) and singlet oxygen ($^1O_2$) could be generated by using conjugated porous polymers under visible light irradiation.[29, 43] Here, spin trap EPR measurements were conducted using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) as superoxide and singlet oxygen trapping agents, respectively. Interestingly, as shown in Figure S7 in ESI, only one oxygen species, $O_2^{\bullet-}$ could be determined by using PCP-MF as photocatalyst. It indicates that $O_2^{\bullet-}$ played a major role for the hydroxylation of boronic acid in this study, similar to previous report,[39] To fully understand the specific role of the photogenerated electron-hole pairs during the photocatalytic hydroxylation reaction, we then added benzoquinone (BQ) as $O_2^{\bullet-}$ scavenger into the reaction mixture, a yield of 45% was determined (entry 6). Both results indicate that superoxide radical anion took a vital part in the hydroxylation reaction of phenylboronic acid. Fluorescence quenching experiment showed that the fluorescence of PCP-

MF could be effectively quenched in the presence of O_2 and phenylboronic acid, indicating an oxidative quenching process (Figure S8 and S9 in ESI). Based on our observations from the screening and control experiments, we propose a modified reaction mechanism similar to the literature.[40, 43]

The proposed mechanism of the hydroxylation of arylboronic acids is illustrated in Figure 2. Upon light exposure, the photoexcited electron is quenched by oxygen, forming the superoxide radical anion $O_2^{\bullet-}$. As the reduction potential of the $O_2/O_2^{\bullet-}$ lies at -0.57 V *vs* SCE,[44-47] the LUMO level of PCP-MF (-0.75 V vs. SCE) was indeed sufficient to activate the molecular oxygen species. The superoxide radical anion then reacts with the boronic acid to form the peroxide radical **A** as intermediate. Meanwhile, triethylamine is oxidized by losing an electron to the photogenerated hole in the excited state of PCP-MF, which returns to its ground state and complete the photoredox cycle. The intermediate **A** then abstracts one H atom from the cationic radical of triethylamine to form intermediate peroxide **B**, which rearranges to form phenyl dihydrogen borate **C**. The final product is obtained after hydroxylation of **C**.

The scope of the visible light-induced oxidative hydroxylation of arylboronic acids is summarized in Table 2. With PCP-MF as photocatalyst, various arylboronic acids, bearing either electron-donating group such as methoxy, biphenyl and naphthalenyl or electron withdrawing groups such as cyano, fluoride, bromide, nitro and cyanomethyl, were effectively oxidized to the corresponding aryl alcohols in good to excellent yields. Notably, the electron-deficient arylboronic acids reacted slightly faster than that of electron-rich ones. A possible explanation is that phenylboronic acids with electron-withdrawing substituents had a higher electron affinity than the ones with electron-donating substituents. This makes them thermodynamically more favorable to complex with superoxide radical, as indicated in the reaction mechanism. Hydroquinone could also be obtained from the relevant *p*-phenylenediboronic acid with a moderate yield (table 2, entry 15). Moreover, repeating experiments for hydroxylation of phenylboronic acid showed a slight decrease with a generally high conversion of more than 80 % during the whole repeating cycles (Figure S10 in ESI). The small decrease of conversion is possibly due to the recovery problem because the polymer demonstrated a very fine powder-like shape, which made some unavoidable loss during the collecting process. Nevertheless, the SEM image of PCP-MF after the fifth cycle barely showed any change compared with the pristine one (Figure S11 in ESI), indicating the stability of the PCP-MF during the photocatalytic reaction.

Conclusion

In summary, a porous conjugated polymer was synthesized via a simple metal-free Knoevenagel condensation reaction at mild conditions. The photocatalytic activity of the porous polymer as heterogeneous photocatalyst was demonstrated by the hydroxylation of a series of arylboronic acids to the corresponding phenols under visible light. High functional group tolerance of the substrates was demonstrated during the photocatalytic reaction. We hope this work can present a new alternative metal-free synthetic route of pure organic and heterogeneous photocatalyts based on porous conjugated polymers at mild conditions and stimulate further discussions in the field.

Acknowledgement

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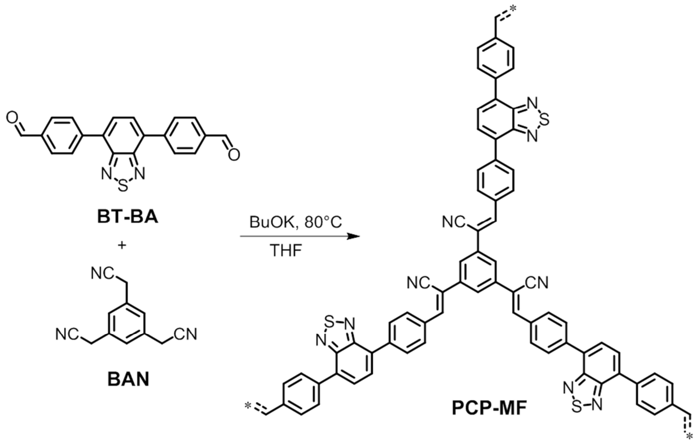


Scheme 1. Synthetic route of the porous conjugated polymer PCP-MF via a simple metal-free Knoevenagel polycondensation reaction.

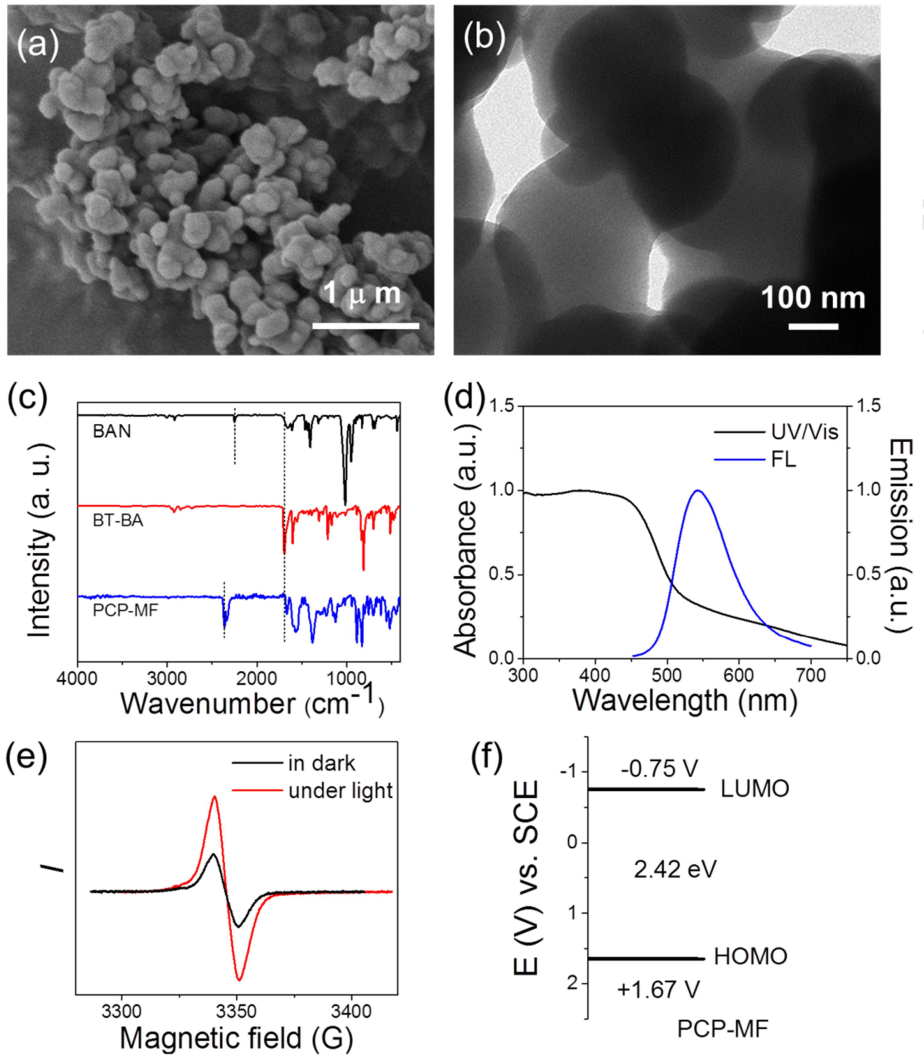


Figure 1. (a) SEM and (b) TEM images, (c) FT-IR spectra, (d) UV/vis DR and fluorescence spectra, (e) EPR spectra in dark and under light irradiation, and (f) HOMO and LUMO band positions of PCP-MF.

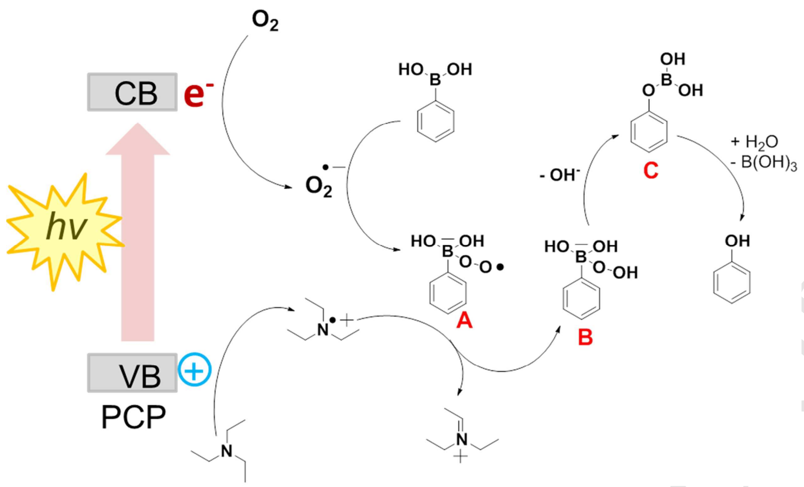


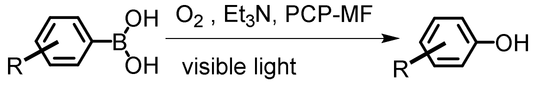
Figure 2. Proposed mechanism of the photocatalytic hydroxylation of arylboronic acids using PCP-MF.

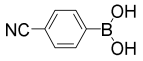
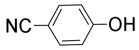
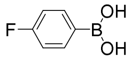
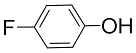
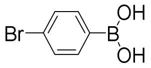
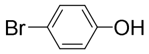
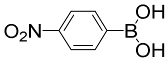
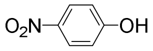
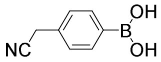
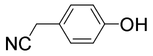
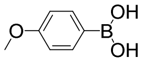
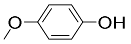
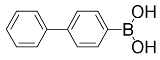
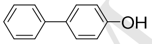
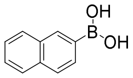
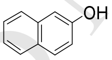
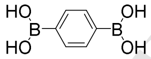
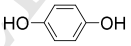
Table 1. Screening and control experiments of the photocatalytic hydroxylation of phenylboronic acid[a]

Entry	Reaction condition variations	Light	Yield[b] (%)
1	-	+	94
2[c]	-	-	<5
3	no Et_3N	+	Trace
4[d]	no O_2	+	Trace
5	no photocatalyst	+	Trace
6[e]	radical scavenger	+	45

[a] Reaction conditions: phenylboronic acid (0.5 mmol), Et_3N (1.5 mmol), photocatalyst (10 mg), 3 mL CH_3CN, 1 atm O_2, 10 hr, white LED lamp (1.2 W/cm^2). [b] Isolated yield after chromatography over silica. [c] In dark. [d] Under N_2 environment. [e] Benzoquinone (BQ) used as radical scavenger

Table 2. Photocatalytic hydroxylation of various arylboronic acids using PCP-MF as photocatalyst[a]



Entry	Arylboronic acid	Product	Time (h)	Yield^b (%)
7			20	96
8			20	92
9			23	88
10			19	95
11			24	85
12			24	93
13			24	95
14			20	83
15			24	76

^{a}Standard reaction conditions: arylboronic acid (0.5 mmol), Et_3N (1.5 mmol), PCP-MF (10 mg), 3 mL CH_3CN, 1 atm O_2, white LED lamp (1.2 W/cm^2). ^{b}Isolated yield after chromatography over silica.

References:

[1] G. Ciamician, The Photochemistry of the Future, Science 36(926) (1912) 385-94.

[2] D.A. Nagib, D.W.C. MacMillan, Trifluoromethylation of arenes and heteroarenes by means of photoredox catalysis, Nature 480(7376) (2011) 224-228.

[3] T.P. Yoon, M.A. Ischay, J.N. Du, Visible light photocatalysis as a greener approach to photochemical synthesis, Nature Chem. 2(7) (2010) 527-532.

[4] J.M.R. Narayanam, C.R.J. Stephenson, Visible light photoredox catalysis: applications in organic synthesis, Chem. Soc. Rev. 40(1) (2011) 102-113.

[5] C.H. Dai, J.M.R. Narayanam, C.R.J. Stephenson, Visible-light-mediated conversion of alcohols to halides, Nature Chem. 3(2) (2011) 140-145.

[6] X.J. Lang, X.D. Chen, J.C. Zhao, Heterogeneous visible light photocatalysis for selective organic transformations, Chem. Soc. Rev. 43(1) (2014) 473-486.

[7] S. Ghosh, N.A. Kouame, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P.H. Aubert, H. Remita, Conducting polymer nanostructures for photocatalysis under visible light, Nat. Mater. 14(5) (2015) 505-511.

[8] X.C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, Nat. Mater. 8(1) (2009) 76-80.

[9] J. Liu, Y. Liu, N.Y. Liu, Y.Z. Han, X. Zhang, H. Huang, Y. Lifshitz, S.T. Lee, J. Zhong, Z.H. Kang, Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway, Science 347(6225) (2015) 970-974.

[10] N. Kang, J.H. Park, K.C. Ko, J. Chun, E. Kim, H.W. Shin, S.M. Lee, H.J. Kim, T.K. Ahn, J.Y. Lee, S.U. Son, Tandem synthesis of photoactive benzodifuran moieties in the formation of microporous organic networks, Angew. Chem. Int. Ed. 52(24) (2013) 6228-32.

[11] K. Zhang, D. Kopetzki, P.H. Seeberger, M. Antonietti, F. Vilela, Surface Area Control and Photocatalytic Activity of Conjugated Microporous Poly(benzothiadiazole) Networks, Angew. Chem. Int. Ed. 52(5) (2013) 1432-1436.

[12] C. Yang, B.C. Ma, L. Zhang, S. Lin, S. Ghasimi, K. Landfester, K.A.I. Zhang, X. Wang, Molecular Engineering of Conjugated Polybenzothiadiazoles for Enhanced Hydrogen Production by Photosynthesis, Angew. Chem. Int. Ed. 55(32) (2016) 9202-9206.

[13] C. Su, R. Tandiana, B. Tian, A. Sengupta, W. Tang, J. Su, K.P. Loh, Visible-Light Photocatalysis of Aerobic Oxidation Reactions Using Carbazolic Conjugated Microporous Polymers, ACS Catal. 6(6) (2016) 3594-3599.

[14] J.X. Jiang, F. Su, A. Trewin, C.D. Wood, N.L. Campbell, H. Niu, C. Dickinson, A.Y. Ganin, M.J. Rosseinsky, Y.Z. Khimyak, A.I. Cooper, Conjugated microporous poly (aryleneethynylene) networks, Angew. Chem. Int. Ed. 46(45) (2007) 8574-8578.

[15] R. Dawson, D.J. Adams, A.I. Cooper, Chemical tuning of CO2 sorption in robust nanoporous organic polymers, Chem. Sci. 2(6) (2011) 1173-1177.

[16] Q. Chen, M. Luo, P. Hammershøj, D. Zhou, Y. Han, B.W. Laursen, C.-G. Yan, B.-H. Han, Microporous Polycarbazole with High Specific Surface Area for Gas Storage and Separation, J. Am. Chem. Soc. 134(14) (2012) 6084-6087.

[17] A. Li, H.X. Sun, D.Z. Tan, W.J. Fan, S.H. Wen, X.J. Qing, G.X. Li, S.Y. Li, W.Q. Deng, Superhydrophobic conjugated microporous polymers for separation and adsorption, Energy Environ. Sci. 4(6) (2011) 2062-2065.

[18] X. Zhuang, Gehrig, D., Forler, N., Liang, H., Wagner, M., Hansen, M., Laquai, F., Zhang, F., Feng, X.3, Conjugated Microporous Polymers with Dimensionality-Controlled Heterostructures for Green Energy Devices, Adv. Mater. 27(25) (2015) 3789-3796.

[19] Y. Xie, T.T. Wang, X.H. Liu, K. Zou, W.Q. Deng, Capture and conversion of CO2 at ambient conditions by a conjugated microporous polymer, Nat. Commun. 4 (2013) 1960.

[20] J.X. Jiang, Y.Y. Li, X.F. Wu, J.L. Xiao, D.J. Adams, A.I. Cooper, Conjugated Microporous Polymers with Rose Bengal Dye for Highly Efficient Heterogeneous Organo-Photocatalysis, Macromolecules 46(22) (2013) 8779-8783.
[21] Z.J. Wang, S. Ghasimi, K. Landfester, K.A.I. Zhang, Photocatalytic Suzuki Coupling Reaction Using Conjugated Microporous Polymer with Immobilized Palladium Nanoparticles under Visible Light, Chem. Mater. 27(6) (2015) 1921-1924.
[22] Z.J. Wang, S. Ghasimi, K. Landfester, K.A.I. Zhang, Highly porous conjugated polymers for selective oxidation of organic sulfides under visible light, Chem. Commun. 50(60) (2014) 8177-8180.
[23] Z.J. Wang, S. Ghasimi, K. Landfester, K.A.I. Zhang, A conjugated porous poly-benzobisthiadiazole network for a visible light-driven photoredox reaction, J. Mater. Chem. A 2(44) (2014) 18720-18724.
[24] Z.J. Wang, S. Ghasimi, K. Landfester, K.A.I. Zhang, Molecular Structural Design of Conjugated Microporous Poly(Benzooxadiazole) Networks for Enhanced Photocatalytic Activity with Visible Light, Adv. Mater. 27(40) (2015) 6265-6270.
[25] Z.J. Wang, K. Garth, S. Ghasimi, K. Landfester, K.A.I. Zhang, Conjugated Microporous Poly(Benzochalcogenadiazole)s for Photocatalytic Oxidative Coupling of Amines under Visible Light, ChemSusChem 8(20) (2015) 3459-3464.
[26] Y.H. Xu, S.B. Jin, H. Xu, A. Nagai, D.L. Jiang, Conjugated microporous polymers: design, synthesis and application, Chem. Soc. Rev. 42(20) (2013) 8012-8031.
[27] F. Vilela, K. Zhang, M. Antonietti, Conjugated porous polymers for energy applications, Energ Environ. Sci. 5(7) (2012) 7819-7832.
[28] R. Dawson, A.I. Cooper, D.J. Adams, Nanoporous organic polymer networks, Prog. Polym. Sci. 37(4) (2012) 530-563.
[29] K. Zhang, D. Kopetzki, P.H. Seeberger, M. Antonietti, F. Vilela, Surface Area Control and Photocatalytic Activity of Conjugated Microporous Poly(benzothiadiazole) Networks, Angew. Chem. Int. Ed. 52(5) (2013) 1432-1436.
[30] J. Schmidt, M. Werner, A. Thomas, Conjugated Microporous Polymer Networks via Yamamoto Polymerization, Macromolecules 42(13) (2009) 4426-4429.
[31] G.L. Lu, H.S. Yang, Y.L. Zhu, T. Huggins, Z.J. Ren, Z.N. Liu, W. Zhang, Synthesis of a conjugated porous Co(II) porphyrinylene-ethynylene framework through alkyne metathesis and its catalytic activity study, J. Mater. Chem. A 3(9) (2015) 4954-4959.
[32] L.B. Sun, Z.Q. Liang, J.H. Yu, R.R. Xu, Luminescent microporous organic polymers containing the 1,3,5-tri(4-ethenylphenyl)benzene unit constructed by Heck coupling reaction, Polym. Chem. 4(6) (2013) 1932-1938.
[33] V. Senkovskyy, I. Senkovska, A. Kiriy, Surface-Initiated Synthesis of Conjugated Microporous Polymers: Chain-Growth Kumada Catalyst-Transfer Polycondensation at Work, ACS Macro Lett. 1(4) (2012) 494-498.
[34] J. Schmidt, J. Weber, J.D. Epping, M. Antonietti, A. Thomas, Microporous Conjugated Poly(thienylene arylene) Networks, Adv. Mater. 21(6) (2009) 702-705.
[35] P. Kuhn, M. Antonietti, A. Thomas, Porous, covalent triazine-based frameworks prepared by ionothermal synthesis, Angew. Chem. Int. Ed. 47(18) (2008) 3450-3453.
[36] F.o. Diederich, P.J. Stang, Metal-catalyzed cross-coupling reactions, Wiley-VCH, New York, 1998.
[37] C. Xu, N. Hedin, Synthesis of microporous organic polymers with high CO2-over-N-2 selectivity and CO2 adsorption, J. Mater. Chem. A 1(10) (2013) 3406-3414.
[38] M.G. Schwab, M. Hamburger, X.L. Feng, J. Shu, H.W. Spiess, X.C. Wang, M. Antonietti, K. Mullen, Photocatalytic hydrogen evolution through fully conjugated poly(azomethine) networks, Chem. Commun. 46(47) (2010) 8932-8934.

[39] Y.Q. Zou, J.R. Chen, X.P. Liu, L.Q. Lu, R.L. Davis, K.A. Jorgensen, W.J. Xiao, Highly Efficient Aerobic Oxidative Hydroxylation of Arylboronic Acids: Photoredox Catalysis Using Visible Light, Angew. Chem. Int. Ed. 51(3) (2012) 784-788.
[40] S.P. Pitre, C.D. McTiernan, H. Ismaili, J.C. Scaiano, Mechanistic Insights and Kinetic Analysis for the Oxidative Hydroxylation of Arylboronic Acids by Visible Light Photoredox Catalysis: A Metal-Free Alternative, J. Am. Chem. Soc. 135(36) (2013) 13286-13289.
[41] Y. Wei, W. Chen, X. Zhao, S. Ding, S. Han, L. Chen, Solid-state emissive cyanostilbene based conjugated microporous polymers via cost-effective Knoevenagel polycondensation, Polym. Chem. 7(24) (2016) 3983-3988.
[42] L. Wang, W. Huang, R. Li, D. Gehrig, P.W. Blom, K. Landfester, K.A. Zhang, Structural Design Principle of Small-Molecule Organic Semiconductors for Metal-Free, Visible-Light-Promoted Photocatalysis, Angew. Chem. Int. Ed. 55(33) (2016) 9783-7.
[43] J. Luo, X. Zhang, J. Zhang, Carbazolic Porous Organic Framework as an Efficient, Metal-Free Visible-Light Photocatalyst for Organic Synthesis, ACS Catal. 5(4) (2015) 2250-2254.
[44] P.M. Wood, The potential diagram for oxygen at pH 7, Biochem. J 253(1) (1988) 287-289.
[45] P.S. Rao, E. Hayon, Experimental determination of the redox potential of the superoxide radical •O2−, Biochem. Biophys. Res. Commun. 51(2) (1973) 468-473.
[46] P.S. Rao, E. Hayon, Redox potentials of free radicals. IV. Superoxide and hydroperoxy radicals . O2- and . HO2, J. Phys. Chem. 79(4) (1975) 397-402.
[47] S. Ghosh, N.A. Kouamé, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P.-H. Aubert, H. Remita, Conducting polymer nanostructures for photocatalysis under visible light, Nature Mater. 14(5) (2015) 505-511.

Highlights

- metal-free preparation of porous conjugated polymers
- photocatalytic oxidative hydroxylation of arylboronic acids
- visible light photocatalysis
- high functional group tolerance of the substrates