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Mild selective photochemical oxidation of an organic sulfide using OxP-polyimide porous polymers as singlet oxygen generators

Jan Hynek[a*], Daniel T. Payne[b**], Lok Kumar Shrestha[a,c], Mandeep K. Chahal[a***], Renzhi Ma[a], Jiang Dong[d], Katsuhiko Ariga[a,e], Yusuke Yamauchi[a,d,f] and Jonathan P. Hill[a]

[a]Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan;
[b]International Center for Young Scientists, National Institute for Materials Science (NIMS), Tsukuba, Japan;
[c]Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Ibaraki, Japan;
[d]Department of Materials Process Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan;
[e]Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, Japan;
[f]Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, Australia

ABSTRACT

A series of porous organic polymers based on a singlet oxygen generating oxoporphyrinogen ('**OxP**') has been successfully prepared from a pseudotetrahedral **OxP**-tetraamine precursor (**OxP(4-NH$_2$Bn)$_4$**) by its reaction with tetracarboxylic acid dianhydrides under suitable conditions. Of the compounds studied, those containing naphthalene (**OxP-N**) and perylene (**OxP-P**) spacers, respectively, have large surface areas (~530 m^2 g^{-1}). On the other hand, the derivative with a simple benzene spacer (**OxP-B**) exhibits the best $^1O_2$ generating capability. Although the starting **OxP**-tetraamine precursor is a poor $^1O_2$ generator, its incorporation into **OxP** POPs leads to a significant enhancement of $^1O_2$ productivity, which is largely due to the transformation of NH_2 groups to electron-withdrawing diimides. Overall $^1O_2$ production efficacy of **OxP-POP**s under irradiation by visible light is significantly improved over the common reference material **PCN-222**. All the materials **OxP-B**, **OxP-N** and **OxP-P** promote oxidation of thioanisole involving conversion of ambient triplet state oxygen to singlet oxygen under visible light irradiation and its reaction with the sulfide. Although the reaction rate of the oxidation promoted by **OxP** POPs is generally lower than for conventional materials (such as **PCN-222**) or previously studied **OxP** derivatives, undesired overoxidation of the substrate to methyl phenyl sulfone is suppressed. For organic sulfides, selectivity of oxidation is especially important for detoxification of mustard gas (bis(2-chloroethyl)sulfide) or similarly toxic compounds since controlled oxidation leads to the low toxicity bis(2-chloroethyl)sulfoxide while overoxidation leads to intoxification (since bis(2-chloroethyl)sulfone presents greater toxicity to humans than the sulfide substrate). Therefore, **OxP** POPs capable of promoting selective oxidation of sulfides to sulfoxides have excellent potential to be used as mild and selective detoxification agents.

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Singlet oxygen generation; oxoporphyrinogen; porous polymer; selective oxidation; organic sulfide

CONTACT Lok Kumar Shrestha SHRESTHA.Lokkumar@nims.go.jp; Jonathan P. Hill Jonathan.HILL@nims.go.jp Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
*Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež 1001, Řež 250 68, Czech Republic.
**School of Life, Health and Chemical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom.
***School of Chemistry and Forensic Science, University of Kent, Canterbury, CT2 7NH, United Kingdom.

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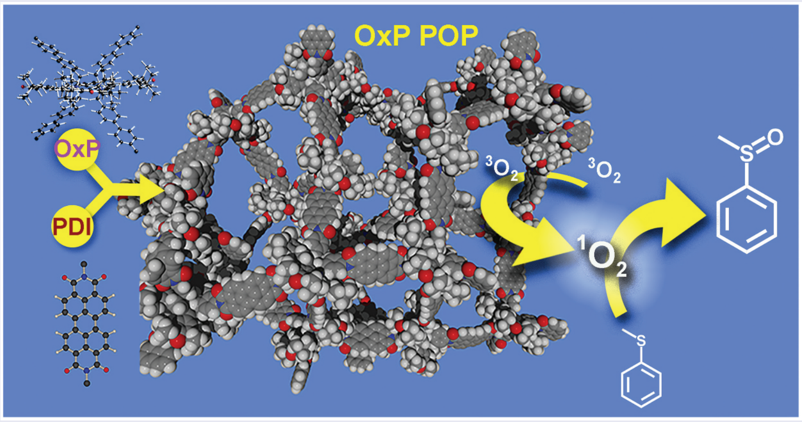

IMPACT STATEMENT

Oxoporphyrinogen (OxP) is a unique chromophore compound in that it is intrinsically de-aggregated allowing large quantum yields of singlet oxygen generation. Due to its structure, OxP is also an ideal building block for porous systems. In this work, we describe the first incorporation of OxP in highly stable microporous polymers strongly enhanced singlet oxygen generation for selective oxidation of organic sulfides to sulfoxides (as a model reaction) under heterogeneous conditions. The novelty of this work lies in the high stability and easy recovery of the materials, the synergetic enhancement of singlet oxygen generation in the polymers over the starting OxP, and the excellent selectivity for the oxidation reaction.

1. Introduction

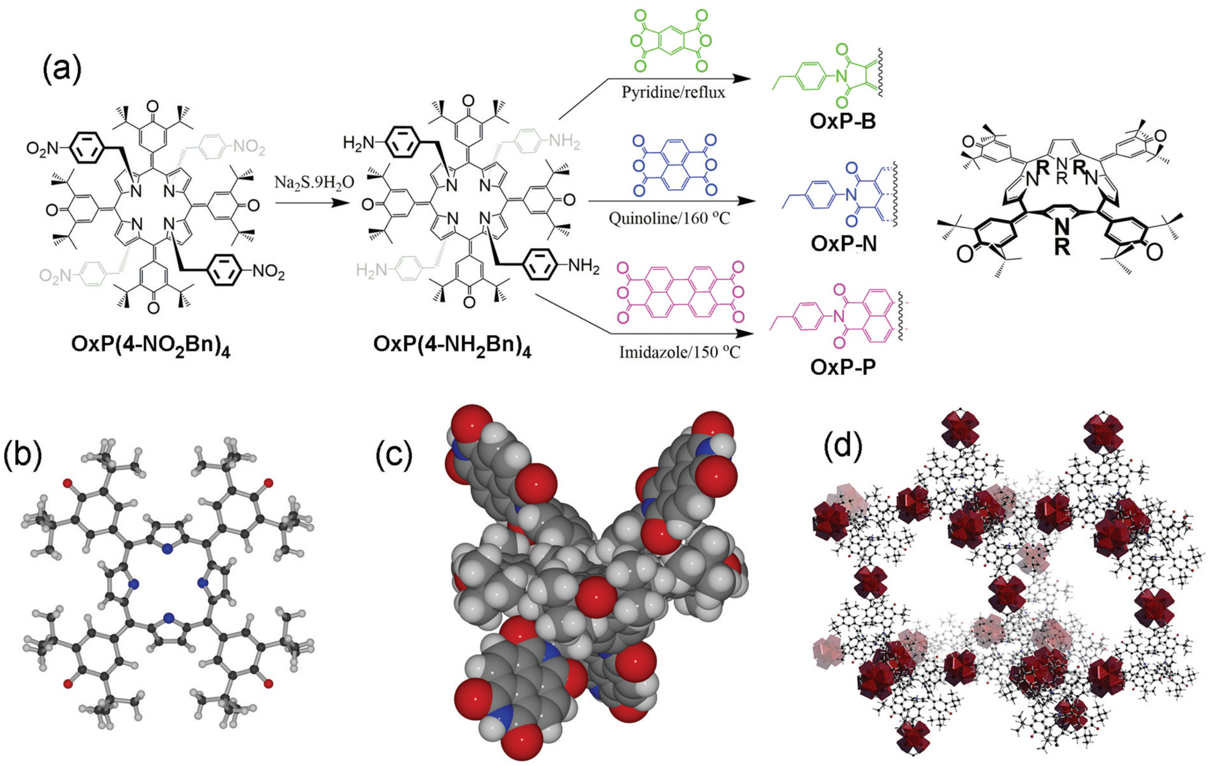

Figure 1. Synthesis and structures of **OxP** polyimide polymer singlet oxygen generators. (a) Synthesis and chemical structures of **OxP** POPs. (b) X-ray crystal structure of **OxP** [53]. (c) Space-filling representation of the energy-minimized (MM2) structure of the substituted **OxP** unit in **OxP-B**. Note the approximately tetrahedral disposition of its N-substituents [47]. (d) Diamondoid porous structure of **OxP-ZrMOF** previously studied for its singlet oxygen generation properties [52]. Panel (d) reproduced by permission from [52], copyright [2021, Elsevier Ltd].

2. Results and discussion

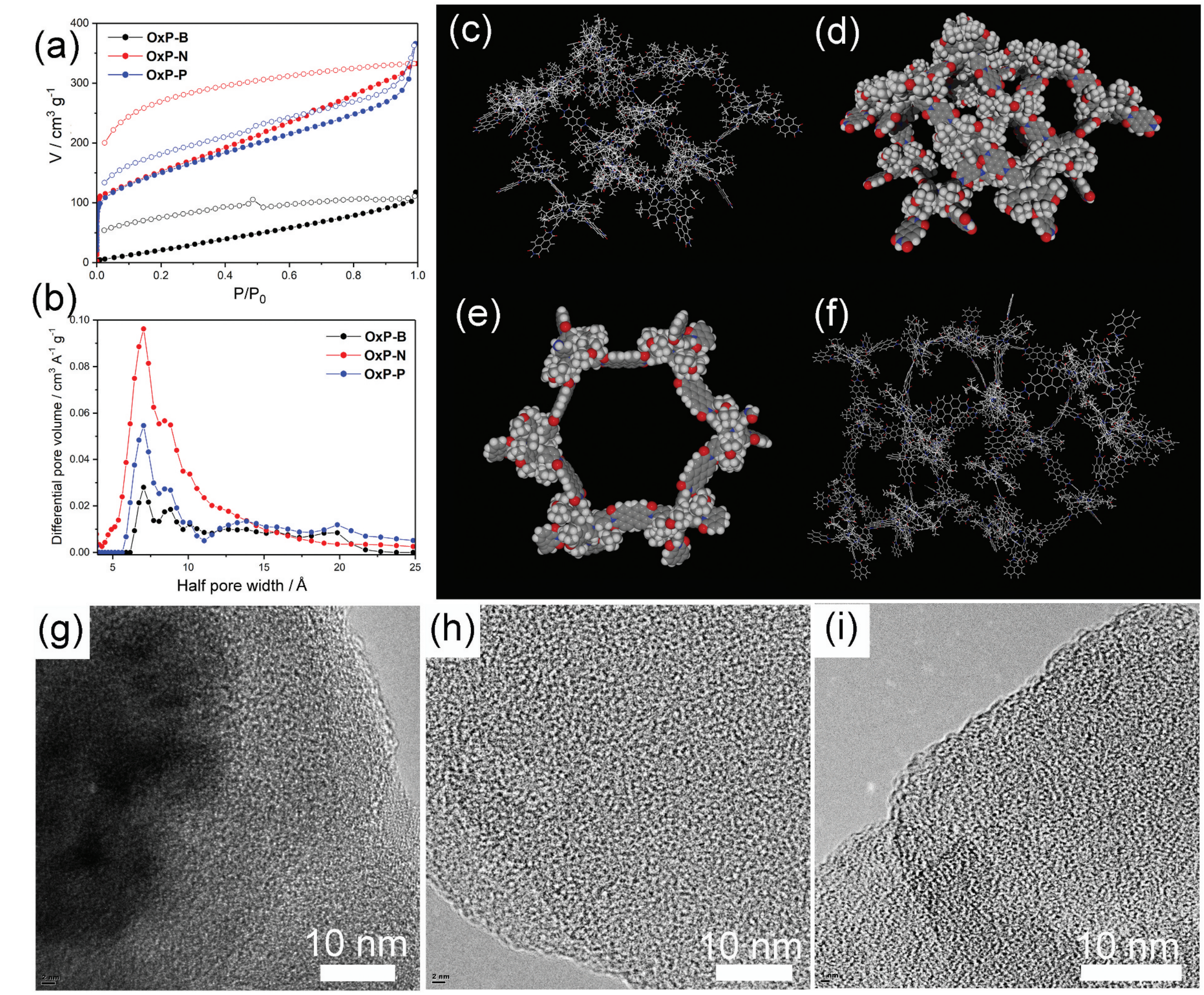

Figure 2. Textural parameters, simulated structures and TEM morphologies of **OxP** POPs. (a) N_2 adsorption isotherms of the **OxP** POPs measured at 77 K. (b) DFT pore size distributions calculated from the N_2 adsorption isotherms. Note that **OxP-N** has the largest proportion of pores in the 5–10 Å range while **OxP-P** and **OxP-B** have increasing proportions of larger pores in the 10–20 Å range. (c) Energy-minimized structure of a nanoparticle of **OxP-N** of approx. 10 nm diameter showing availability of pores based on rigid molecular components. (d) Space-filling representation of the **OxP-N** structure in (c). (e) Stable (energy-minimized) hexagonal pore structure (diameter 4 nm approx.) possible in **OxP-P** polymer. (f) Energy-minimized structure of a nanoparticle of **OxP-P** of approx. 10 nm diameter showing availability of pores based on rigid molecular components. TEM micrographs of (g) **OxP-B**, (h) **OxP-N**, and (i) **OxP-P** revealing amorphous microporous morphologies for the **OxP** POPs. See figure S5 for low resolution SEM and TEM images of the materials.

Table 1. Textural parameters of the **OxP** POPs studied.

Sample	S_{BET}/m^2 g^{-1}	V_{pore}/cm^3 g^{-1}
OxP-B	132	0.151
OxP-N	534	0.467
OxP-P	532	0.466

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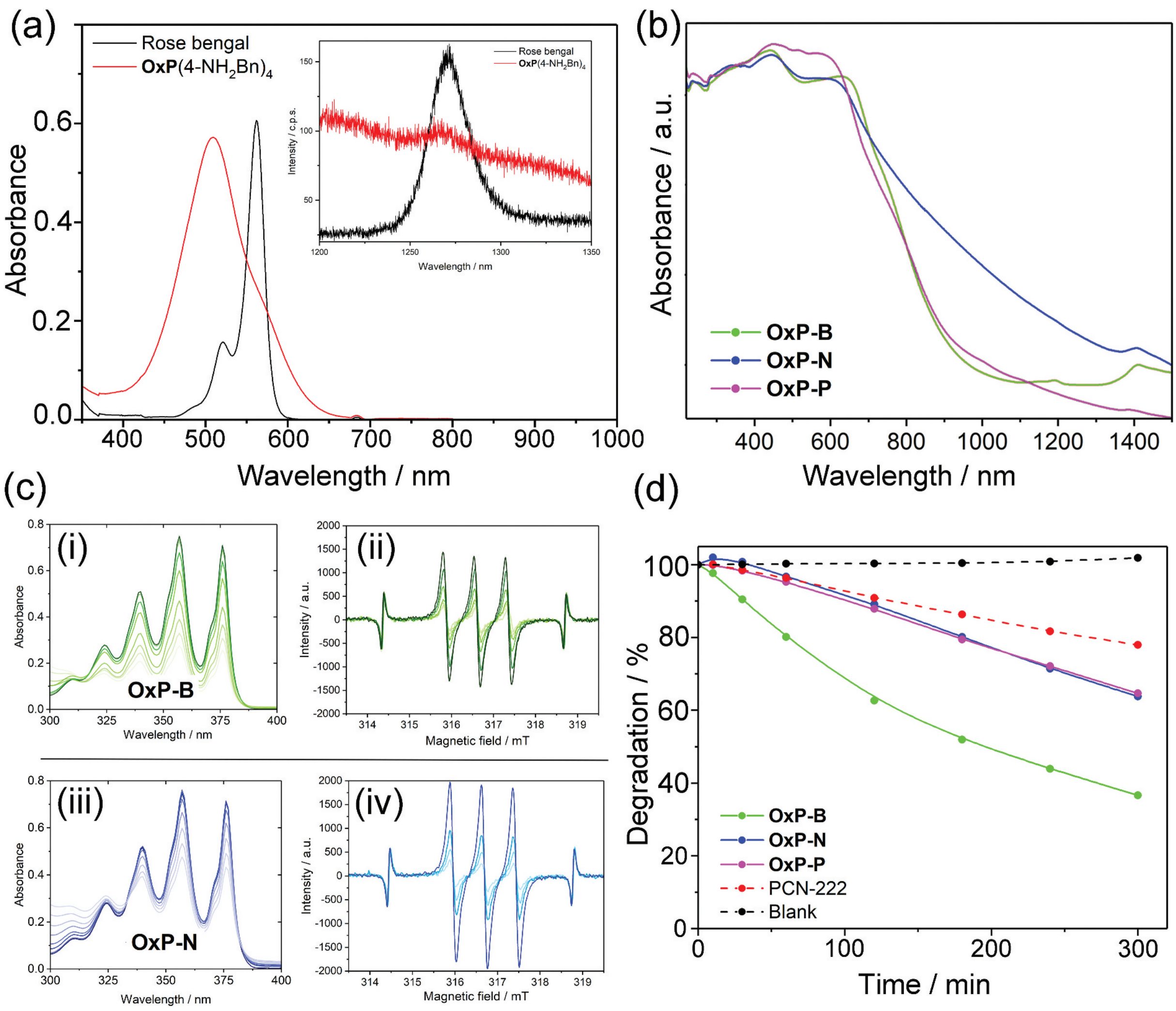

Figure 3. Electronic absorption spectroscopy. (a) UV-vis spectra of POP precursor **OxP(4-NH$_2$Bn)$_4$** and Rose Bengal (used as a reference $^1O_2$ generator in this study). Inset shows the phosphorescence emission peak due to $^1O_2$ generated by the respective dyes. Note the weak peak for **OxP(4-NH$_2$Bn)$_4$** (amines quench $^1O_2$) and the background emission tail due to **OxP** chromophore. (b) Solid state UV-vis spectra of **OxP** POPs. (c) Evidence for effective $^1O_2$ generation by **OxP-B** and **OxP-N**: (i) attenuation of anthracene electronic absorption by endoperoxide formation under irradiation (during 5 h) and (ii) ESR spectra measured in the presence of TEMP spin trap under irradiation in the presence of **OxP-B** POP (during 3 h) and (iii,iv) similar data (measured respectively over 5 h and 2 h periods) in the presence of **OxP-N** POP. (d) Decay in anthracene absorption in the presence of the **OxP** POPs, PCN-222 and without sensitizer (blank).

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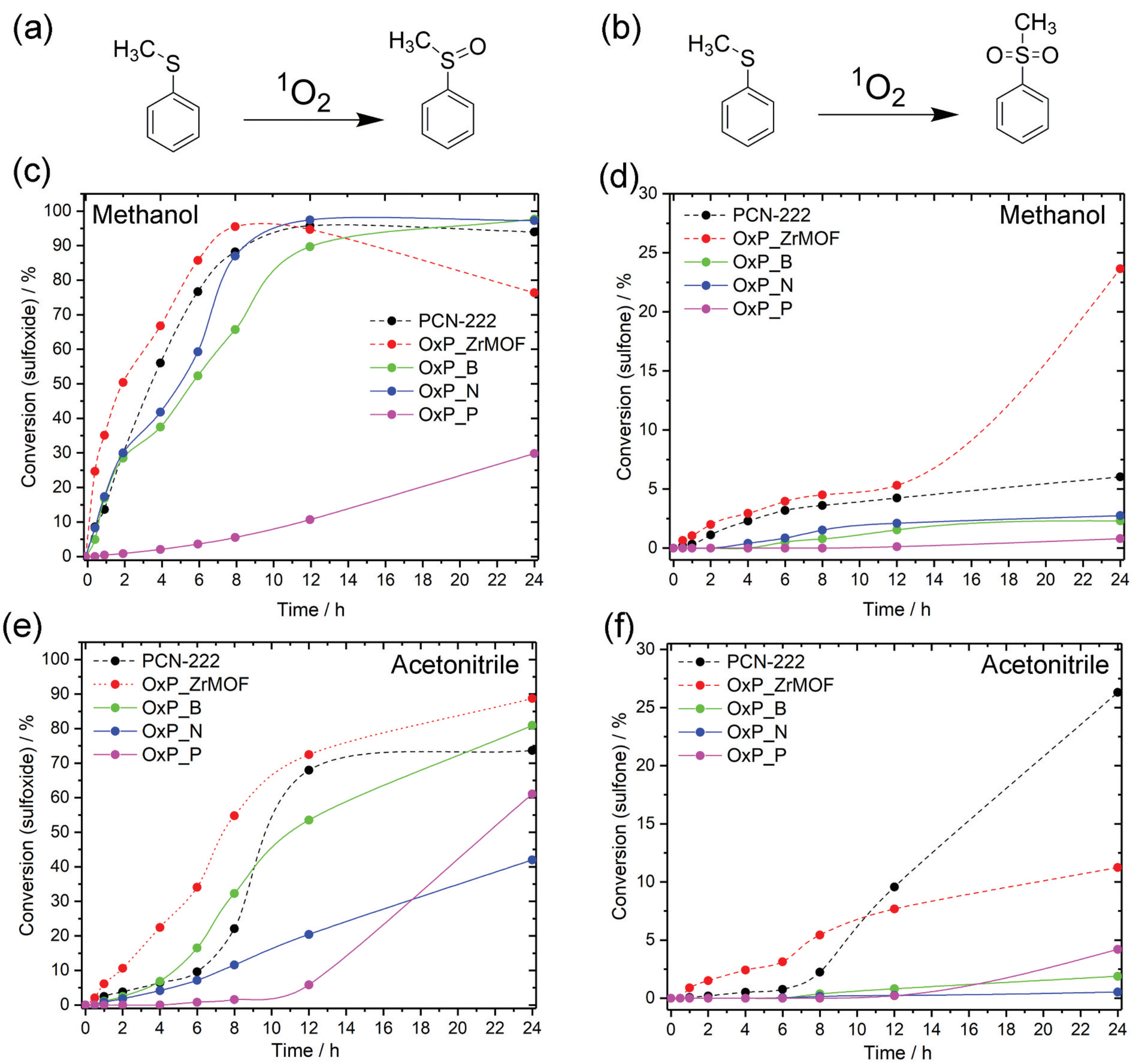

Figure 4. Conversion of thioanisole to its oxidation products by applying **OxP**-POP-generated $^1O_2$. (a) Oxidation of thioanisole to methyl phenyl sulfoxide. (b) Oxidation of thioanisole to methyl phenyl sulfone. (c) Percentage conversion to methyl phenyl sulfoxide for **OxP** POPs (1 mol% based on substrate) suspended with stirring in methanol-d_4 solutions of thioanisole ($c = 0.125$ M) irradiated with broad band visible light during 24 h. (d) Percentage conversion to methyl phenyl sulfone for **OxP** POPs (1 mol% based on substrate) suspended with stirring in methanol-d_4 solutions of thioanisole ($c = 0.125$ M) irradiated with broad band visible light during 24 h. (e) Percentage conversion to methyl phenyl sulfoxide for **OxP** POPs (1 mol% based on substrate) suspended with stirring in acetonitrile-d_3 solutions of thioanisole ($c = 0.125$ M) irradiated with broad band visible light during 24 h. (f) Percentage conversion to methyl phenyl sulfone for **OxP** POPs (1 mol% based on substrate) suspended with stirring in acetonitrile-d_3 methanol-d_4 solutions of thioanisole ($c = 0.125$ M) irradiated with broad band visible light during 24 h. Conversion was estimated using ^1H NMR spectroscopy after diluting (with $CDCl_3$) aliquots of the reaction mixture.

Table 2. Photocatalysts (**OxP-N**) stability for use in batch selective oxidation reactions.

Reaction run[a]	Conversion[b]/%	Yield (sulfoxide)
1	99.1	97.6
2	99.6	97.1
3	99.6	97.3
4	99.8	97.3
5	99.3	97.6

[a]For five consecutive 12 h reactions with photocatalyst recycling. [b]Based on integration of NMR peaks due to products (sulfoxide (2.74 ppm), sulfone (3.06 ppm)) and residual thioanisole (2.47 ppm).

3. Conclusion

Acknowledgments

Disclosure statement

Funding

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References

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