



Kent Academic Repository

Hynek, Jan, Payne, Daniel T., Shrestha, Lok Kumar, Chahal, Mandeep Kaur, Ma, Renzhi, Dong, Jiang, Ariga, Katsuhiko, Yamauchi, Yusuke and Hill, Jonathan P. (2024) *Mild selective photochemical oxidation of an organic sulfide using OxP-polyimide porous polymers as singlet oxygen generators*. *Science and Technology of Advanced Materials*, 25 (1). ISSN 1878-5514.

Downloaded from

<https://kar.kent.ac.uk/107250/> The University of Kent's Academic Repository KAR

The version of record is available from

<https://doi.org/10.1080/14686996.2024.2322458>

This document version

Publisher pdf

DOI for this version

Licence for this version

CC BY-NC (Attribution-NonCommercial)

Additional information

Versions of research works

Versions of Record

If this version is the version of record, it is the same as the published version available on the publisher's web site. Cite as the published version.

Author Accepted Manuscripts

If this document is identified as the Author Accepted Manuscript it is the version after peer review but before type setting, copy editing or publisher branding. Cite as Surname, Initial. (Year) 'Title of article'. To be published in **Title of Journal**, Volume and issue numbers [peer-reviewed accepted version]. Available at: DOI or URL (Accessed: date).

Enquiries

If you have questions about this document contact ResearchSupport@kent.ac.uk. Please include the URL of the record in KAR. If you believe that your, or a third party's rights have been compromised through this document please see our [Take Down policy](https://www.kent.ac.uk/guides/kar-the-kent-academic-repository#policies) (available from <https://www.kent.ac.uk/guides/kar-the-kent-academic-repository#policies>).



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

Jan Hynek, Daniel T. Payne, Lok Kumar Shrestha, Mandeep K. Chahal, Renzhi Ma, Jiang Dong, Katsuhiko Ariga, Yusuke Yamauchi & Jonathan P. Hill

To cite this article: Jan Hynek, Daniel T. Payne, Lok Kumar Shrestha, Mandeep K. Chahal, Renzhi Ma, Jiang Dong, Katsuhiko Ariga, Yusuke Yamauchi & Jonathan P. Hill (2024) Mild selective photochemical oxidation of an organic sulfide using OxP-polyimide porous polymers as singlet oxygen generators, Science and Technology of Advanced Materials, 25:1, 2322458, DOI: [10.1080/14686996.2024.2322458](https://doi.org/10.1080/14686996.2024.2322458)

To link to this article: <https://doi.org/10.1080/14686996.2024.2322458>



© 2024 The Author(s). Published by National Institute for Materials Science in partnership with Taylor & Francis Group.



[View supplementary material](#)



Published online: 01 Mar 2024.



[Submit your article to this journal](#)



Article views: 960



[View related articles](#)



[View Crossmark data](#)

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^c, Mandeep K. Chahal^{a***}, Renzhi Ma^a, Jiang Dong^d, Katsuhiko Ariga^e, Yusuke Yamauchi^{a,d,f} and Jonathan P. Hill^a

^aResearch Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan;

^bInternational Center for Young Scientists, National Institute for Materials Science (NIMS), Tsukuba, Japan;

^cDepartment of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Ibaraki, Japan;

^dDepartment of Materials Process Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan;

^eDepartment of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, Japan;

^fAustralian 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-NH₂Bn)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 m² g⁻¹). On the other hand, the derivative with a simple benzene spacer (OxP-B) exhibits the best ¹O₂ generating capability. Although the starting OxP-tetraamine precursor is a poor ¹O₂ generator, its incorporation into OxP POPs leads to a significant enhancement of ¹O₂ productivity, which is largely due to the transformation of NH₂ groups to electron-withdrawing diimides. Overall ¹O₂ production efficacy of OxP-POPs 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 intoxication (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.

ARTICLE HISTORY




Received 22 November 2023

Accepted 17 February 2024

Revised 26 January 2024

KEYWORDS

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-Rež 1001, Rež 250 68, Czech Republic.

**School of Life, Health and Chemical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom.

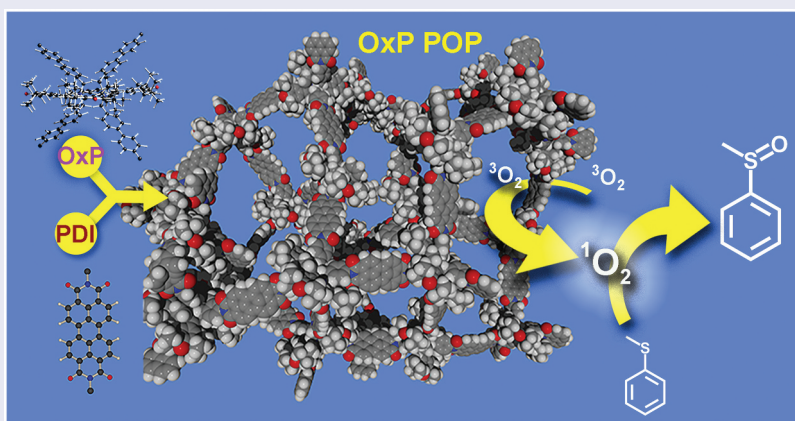
***School of Chemistry and Forensic Science, University of Kent, Canterbury, CT2 7NH, United Kingdom.

This article has been corrected with minor changes. These changes do not impact the academic content of the article.

 Supplemental data for this article can be accessed online at <https://doi.org/10.1080/14686996.2024.2322458>.

© 2024 The Author(s). Published by National Institute for Materials Science in partnership with Taylor & Francis Group.

This is an Open Access article distributed under the terms of the Creative Commons Attribution-NonCommercial License (<http://creativecommons.org/licenses/by-nc/4.0/>), which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.



IMPACT STATEMENT

Oxoporphyrinogen (OxP) is a unique chromophore compound in that it is intrinsically deaggregated 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

! 3 . # \$ " # # 3

" # \$! # # 3

%&' # (#) # % " ! 3

* # +#, # (/ 3

" -# . / # 9 : 36 /3

0 ")# .#)# .3 5 (3

' 7% 5 " ; " #

" " 6 / # "

1 2 # " * , #

4 3 1 3 # 3

\$ # (' % % + 7 1 # % % 3

" 3 3 3

)# * # " 5 6 / - %&' , # 3

% % , # " 3 # 3 , #

' 3 3 1 3

" - ' 3 < 3 \$ % % 6 / \$ #

8 3 5 % % 7 / \$\$ 3

6 / 7 / 3

),) ! # " 3
 5 7 \$ (# \$) # 3
 \$* 0 \$+ #
 # 0) ' " ?).. 3 5 3
 % % # 1 0) ' 3 5 3
 " # " 3
 #(#)#, 3 0 ' " 3
 3 % % " 3
 \$, 8 39 : 6 / 3
 # % % \$- # 3 / " @3
 (. # (3 / % % # / "\$ "
 (\$ # # " (3 5 / 3
 3 5 % % = < 5)# . #)# . 3 # "
 5 \$)# 3 3 3 3(3 # "
 ((3 # " / 3 # "
 (() " >3; / " 3 39
 (* (+ / " 3 39
 (, # (- #)

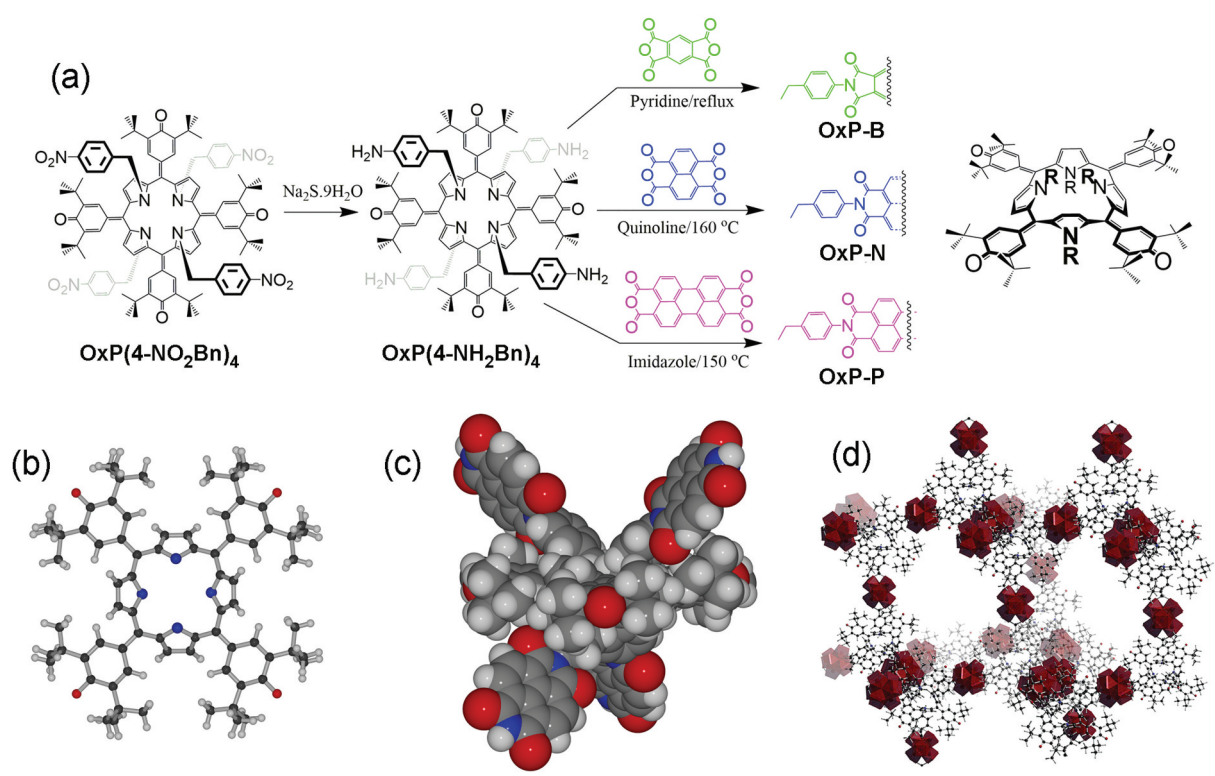


Figure 1. Synthesis and structures of **OxP** polyimide polymer singlet oxygen generators. (a) Synthesis and chemical structures of **OxP** POPs. (b) X-ray crystal structure of **OxP** [53]. (c) Space-filling representation of the energy-minimized (MM2) structure of the substituted **OxP** unit in **OxP-B**. 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

7 ' " 3
 7 ; " 3
 % % " 5# " " 5 3
 (3 0 3 / 8 0 , " 3
 >3)(# " 3 B&@ / (" 3
 3>3 0 # 7H 3
 >3 0 3 " *)H)H I / # 3
 ! 3 5 # " " \$ 5 \$)H / #> 3
 3 3 0 (D) 0 I 3
 % % A 0 # 3
 # A B # 3
 A 1 0 / # 3 J) B&@ " 3
 # " " 3 K 9 # " 0 3
 #(#)#,3 # " " 3
 1 *.c7) / 3\$(#-# .3 ' > 3 % % " 8
 " " " 3 / 3
 # 0 9 8 3 ' " " # 5 3
 \$(#-# .3 @! & % % / # \$. E " " 3
 " 5 # " 0 " ; " # 3
 5)) ')\$. E # " 3
 5 / + .D +\$. E # "), ' 5
 3 7A +, . E # " 3
 > D ; \$..D\$).. E ' > 3 0 " 3
 , " 7A D >; > 3
 5 +\$. * , . E 8 # 0 &/' 3
)*)+ 8 /)D . L / # .D 3
 &F / \$ #)G 0 # 3
 0 " ")G . L & # " 3
 ... G &F & % % 1 # " 3
 # 0 D* G / " 5 ' 5 3
 " ")D) % % " 3
 G B % % " 0

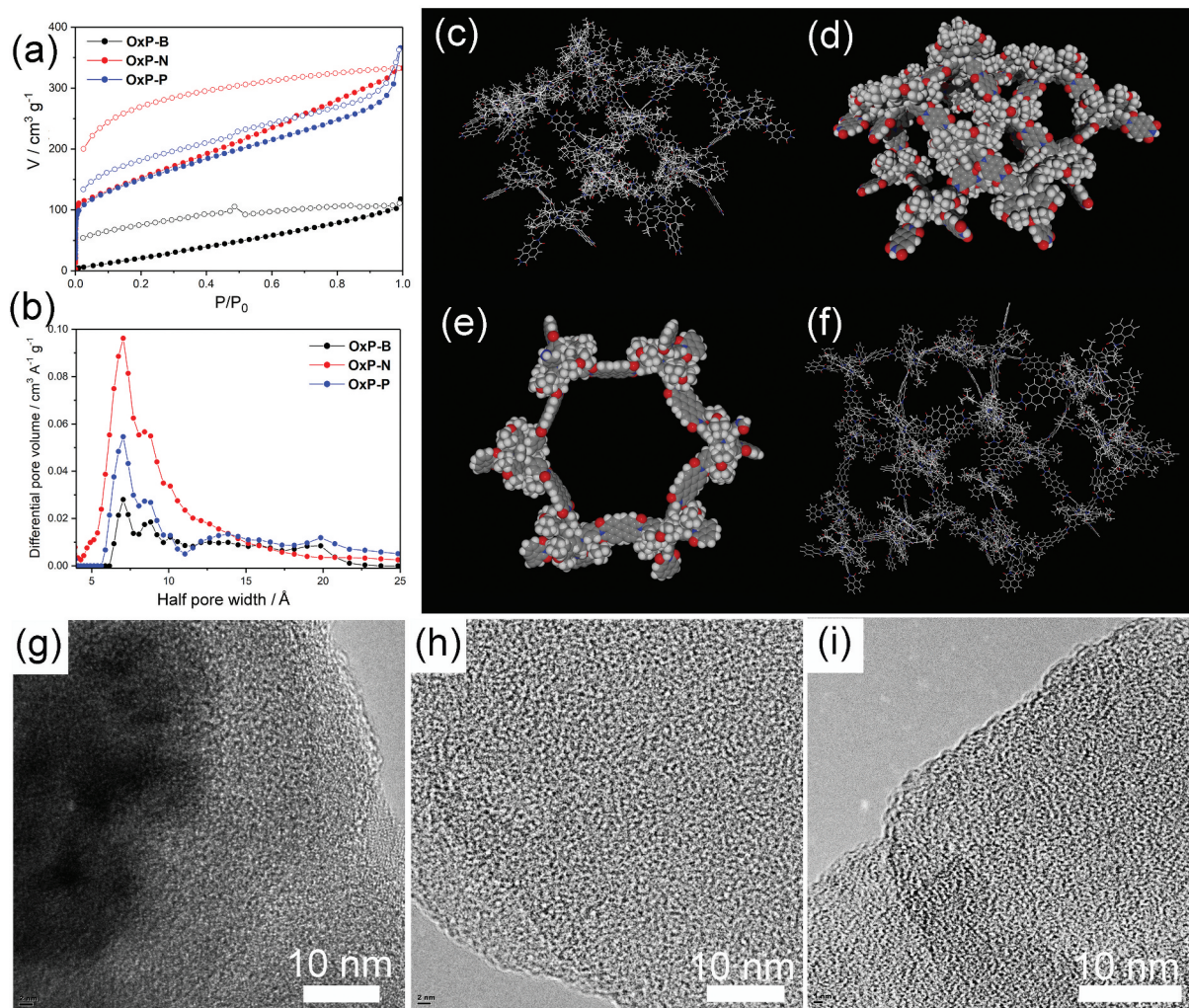


Figure 2. Textural parameters, simulated structures and TEM morphologies of **OxP** POPs. (a) N_2 adsorption isotherms of the **OxP** POPs measured at 77 K. (b) DFT pore size distributions calculated from the N_2 adsorption isotherms. Note that **OxP-N** has the largest proportion of pores in the 5–10 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

3
3
0 # " " "
M 5 % %
2 5 # "
0 " 5 3
" " 6 ' 0 ' 3 /
" 1 " 5 2 N . " "
" # " 0 # " 3
, 0 " " 0 M DB D' MB'

7 / 0 / 1 5 8 # % %
 N(0 ' B6 ' B6 # " " 3
 , 3 0 6 MB' " 3
 " / D ' B6 B 3>3 5
 " /) " B6) . / \$ # " (..
 ' B6 % % ' 3 # 3 *) . ! M # # " #
 #)) .)) % #
 % % +.
 % % !

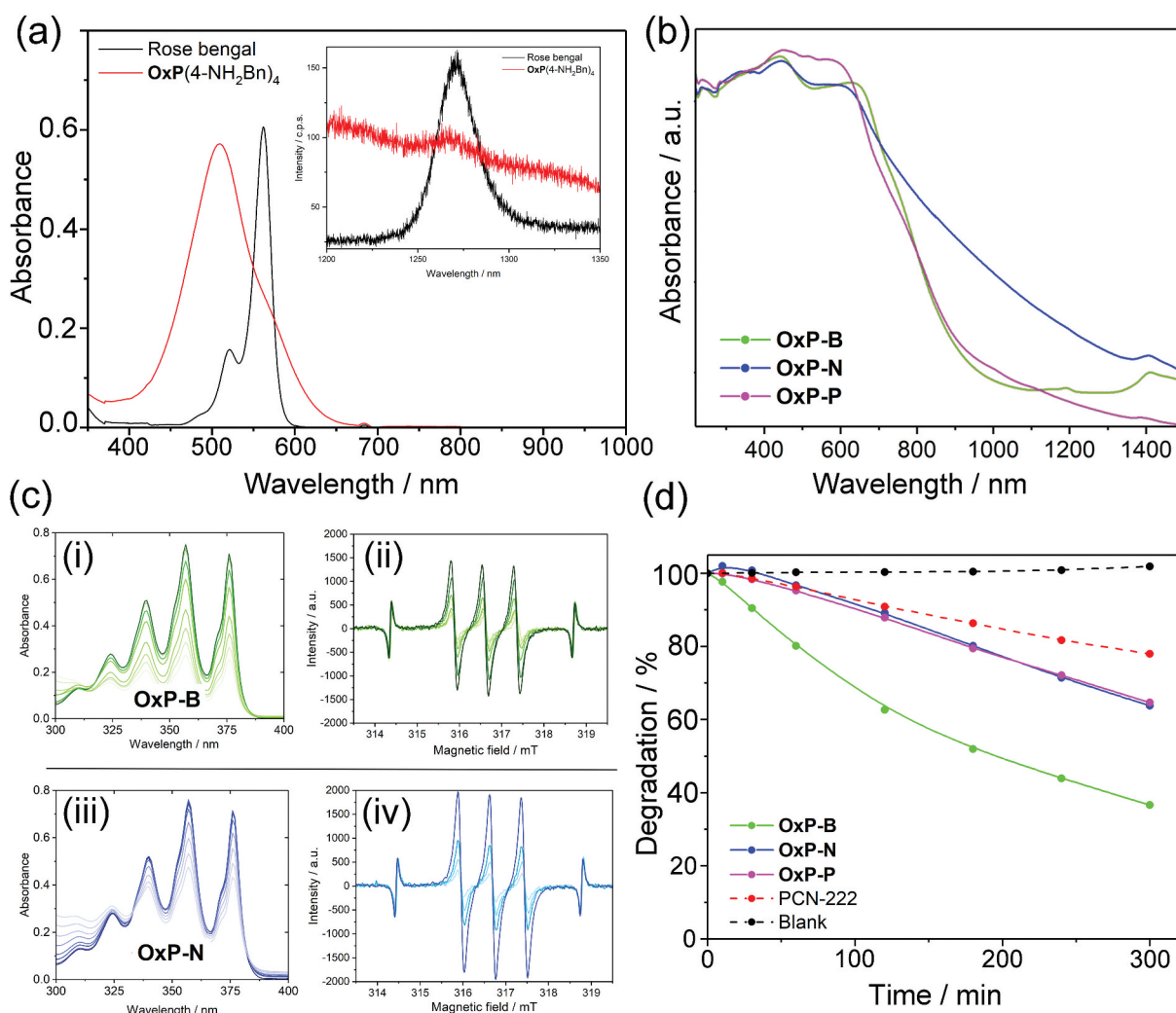


Figure 3. Electronic absorption spectroscopy. (a) UV-vis spectra of POP precursor **OxP(4-NH₂Bn)₄** and Rose Bengal (used as a reference ¹O₂ generator in this study). Inset shows the phosphorescence emission peak due to ¹O₂ generated by the respective dyes. Note the weak peak for **OxP(4-NH₂Bn)₄** (amines quench ¹O₂) and the background emission tail due to **OxP** chromophore. (b) Solid state UV-vis spectra of **OxP** POPs. (c) Evidence for effective ¹O₂ 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).

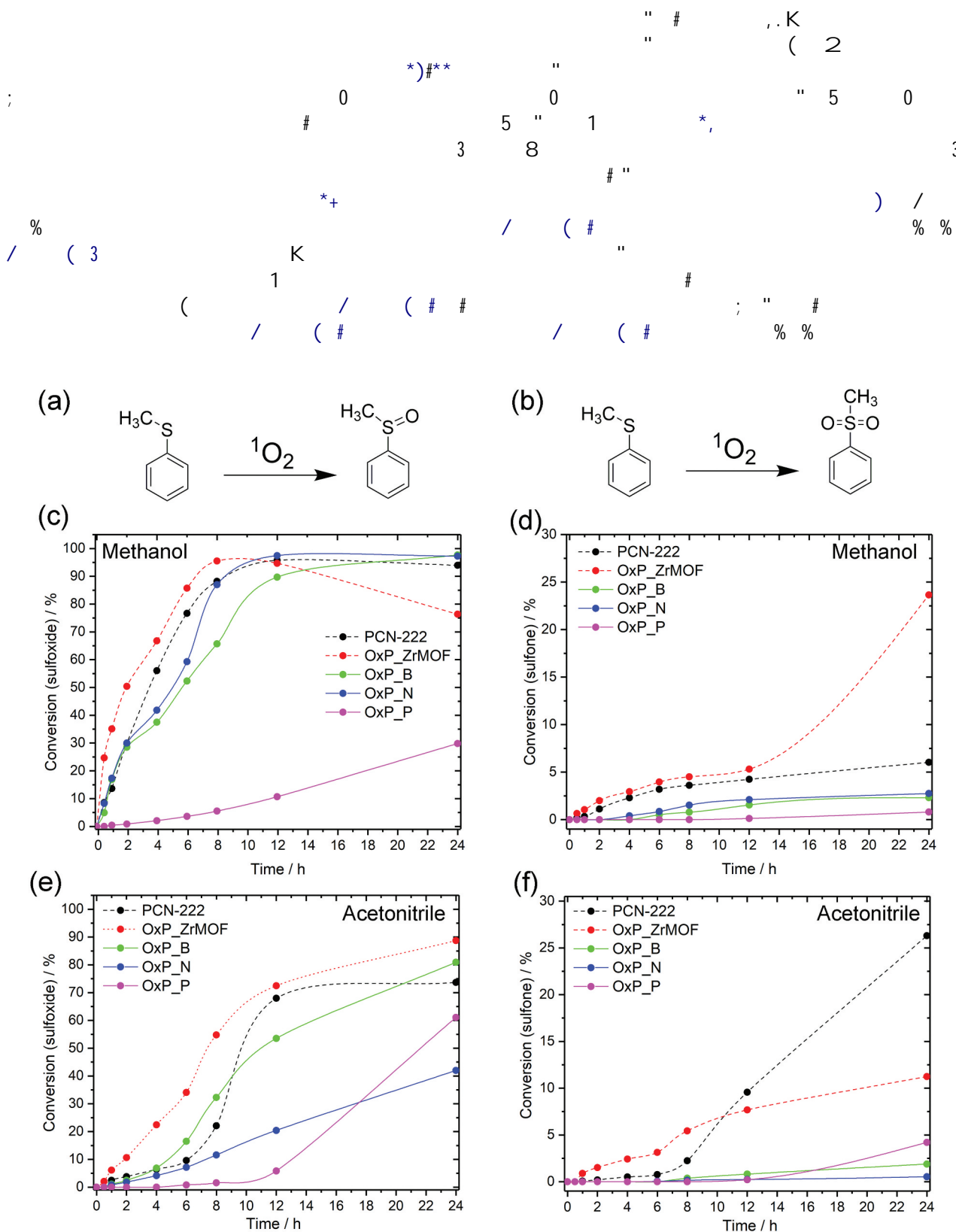


Figure 4. Conversion of thioanisole to its oxidation products by applying OxP-POP-generated 1O_2 . (a) Oxidation of thioanisole to methyl phenyl sulfoxide. (b) Oxidation of thioanisole to methyl phenyl sulfone. (c) Percentage conversion to methyl phenyl sulfoxide for OxP POPs (1 mol% based on substrate) 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.

ORCID

F 5 X ID HSS S...3...\$3 *,.3
* -
X 5 8 ID HSS S...3... 3 ((3 -))

References

& ! 67#7 !T % 0
.. I \$D \$(H\$) D\$+ H . . *S3,)() .
...\$(3*
/ 4 T# U#6 U M 3
4 6 . \$I ,
. H(.,) H . \$\$-.S , .(.,)
\$ & : # X 7 H
H . \$\$,-S . - . *(.
(; 6! % H
" < % %
) 7 # 6 ' # #
D 0 3
% % . ,I +
H (-.D) (H . . \$-S7,%%....,B
* ; 6! 8 3
H " 1 5
7 6 . *I\$H*+D+\$ H . . *S4
+ > 5 U# > 5 8 W
. +I + +H \$. D \$\$* H . . S
+ ... *
, % # M # % 8#%
% H 3
+H)\$D)(+ H . . S . ,...+*
- 2 W2#U U7 ! S
7 ! .. I(, H -)D - , H . . S
. .+\$
. W !' # 7 5 %># 2 T;
& 3"
" 3
0 87
8 6 . \$I) . H . - D . . . H
. . S (. ,+
X T#& &#U F % 0
. +I, (* H,)- D, *. \$ H . . ,*\$ S
; 6! / 0
% H %
. ,I + H))D) \$\$ H . . \$-S
7,%%. -)M
\$ M 3W 0 5 8 > " 3
4 H 3
6 . I () H . -, H . \$\$-.S (.) .-,
(' ' # T7# T 1 ; 7#
%
0 T8 7 . -I (\$- H))(+D))) * H
. . S4 - .)--

) U#2 F#@ 9 6 3 " 5
H
M T . I *H -..\$, H . . . S
. -..\$,
* 6 WW# 8 ; > 3
" 5 0
/ 7 . I .H-+ +(+
H . \$\$,-S . -+ +(+
+ 8 Y T# 6 3M Z ! %
" 5
/ 7
. I-H+., \$ H . \$\$,-S . +., \$
, 9 '# @ W# 7 2# %
H 3
6 7 / . .I(H\$ \$ D\$)\$ H
. . \$-S7-V6..*\$;
- W 3/ &7 03
3 3 " "
7 % . ,I +H) D)\$ (
H . . . S . ,... *
. U 7#U ; #M T# >3
"
. .I)(- H * D *\$. H . . . S
. . - *+
F #9 U#F U# 6 3
8 7 M 3 B
. (I\$(.H \$,. H . . *S4 . \$ \$,.
F #2 2#@ !# 7 3
;
T 7 . I(\$H-- D .. (H . . *S4 .
. . .
\$ U ; #9 F#2 T# 0 3
3M> 3
B 8 . (I\$H-+D . , H . . \$-S
\$.. \$-4
(; 5 T# 7 6X#% &' # % 3
" 5 7
7 ! . .I()H \$)(H . . *S4 . .
\$)(
) / &# W 9U# F T!# 9 3
%7>3 H
D
" 5 " 7 B . I)
3
(H . \$.+D . \$. H . . S . . ((+
* ; 5 T# [Y #M\] 5 &#% %
0 D " 3
" 5 "
7 7 . +I)\$
* H,))D,)*. H . . \$-S7+77.).*,M
+ ; 5 T#! 5^ T# & T# & 3
3 4 "
! 7 8
. *I*). H((+-D((,+ H . . \$-S7*! 8. (.*W
, 9 U# 9 F# 2 9# ! 3
" 5
M . -I \$H -(* H . . *S4
. - -(*
- ; 5 T# 9 5 T#! 5^ T# &
" 5
87 8
6 . ,I . . H,) +D,)\$ H .
. S + ,-\$)

\$. 8 8#7 66#U T# % 3
M & %U3
% %
T 8 7
.I ((\$ H ,)) (D ,)* (H . . S4 . . . + , ()
\$ F U# ; " 8T# ; T' # 3
3 0
D " 5 8 "
7 B .)I) (\$ H-.. D-..) H . . . S
.) . \$+(
\$ U 6#F ; ; 3
" 5
T 8 7 --)I + (H . (. D
. (. H . . S4 .. (* . \$ \$
\$\$ 7_Z 8%#M 8 # 5" >2# 7 H
" 5
..)I\$.)+) H **D +. H . *S
. (.
\$(& U# W T# 2 V# 7
" 5 H S7 /3
F9P 0 5 D6 T 8
7 . I \$ \$ (- H -, *D -, H . . . S
4 . *, (*
\$) ' !2#W 2!#0 F ; 7# /
5
" 5 7 6 .. *I ,
H) -*D)\$. H . . S . * ++
\$* ' !2#6 T#% %T# ,
" 5 8
6 .. ,I . (H +(D +(* H . . . S
.....\$.
\$+ X %# 8 6# ' 8 % #
' 0 3 " 5
8 " 7 B .. ,I(+ , H\$) . D
\$) \$ H . . . S .. +) + .
\$, / X# 5 86# ; MW# #

3 7
6 .. -I (H\$. \$D\$. \$) H . . . S
- .. " "
\$- W T# / Z T6T# / > 3
.. -I) . H . . , D
H . . . S .. + *
(. X %# ; T' # > ' % 3
H 87
7 . I + H, -D, \$) H . . . S .. \$
(> 7T#U 6T# ' & 72# ; 3
3
T ; 0 6 . -I\$**H() D(*) H
. . *S44 0 ' ' .
(; U # U># / 92# & 3
3
" 5 < 7
. I , *H \$ *(* H . . . *S4 .
\$ *(*
(\$ 7 &# F 7# ' T# /
% % 7 . -I . . H * , D
, H . . . \$-S7, %U . * . ;
((6 F! ' , \$I\$- \$ H\$, -) D\$, - , H
. . *S .. (. 3 (. . . - , - 3 .
() X & # T 7 (H 3
" # #
" 7 # !
. (I((H)\$ D)(* H . . . \$-S7(7) . .)+B

(* ; T%# 8F# &< 0 /#
7
>3 7
.. *I() . H, , , D, -* H . . S . *) -
(+ ; T%# ; " T# 8 7B# ; #
>3 3 3
H # 3
T
7 .. (I*- , H) , * D) , *- H . . S4 . (- (.
(, 8# F T# ; T%# >
T 8 7
.. -I \$ H-(-D-(-) H . . . S4 - . \$ \$+
(- 7 6X#% &' # F T#
%3 "
7 H B T . . I *) , H \$ ++D \$, \$ H .
.. S . . . \$ **
) . 7 6X#% &' # 6 U# 6
' 3
3 B T 7
. . I . . H, D- . H . . . S4 . - . + *
) &< 0 /# >X# @ U# 8 3
3 0 3
T 8 7 .. -I \$ ((H * \$, D * (*
H . . S4 - (, \$. *
) ; 5 T#% &' # 7 6X# B
%
6 ' 7 . I H ..) \$(H . . *S4
. . .) \$(
)\$ W 8T# 6 F! # > XM#)# . #)# . 3
6 5 \$#) 3 3 3 3(31 3
H 5 3
T 7 # 7 7 - , -I
H +) D +)\$ H . . \$-S7\$- , - . . . +)
)(6 F! # ; T%# U W /
% , > 3 5
3 5 \$#) 3 3 3 3(3
T ; 7 --) I\$
H +D . H . . S4)) + \$. +
)) / V# 2 T# W # \$&
" 5
T 8 7 .)I \$+ * H, \$) D, \$))
H . . S4) . ((+
)* 7 0 &# W 2# T X# #

5 a 8
" 3 3
6 . \$I , + H - (. H . \$ \$- . S
) + F V# ; 2#% /# %
" T 6 . -I) ()
H +D + H . . . + S , ,) \$3 . , 3 , 3
) , / 4 # & # W X %
% % 6 ; 0
. \$I . . H (. , \$D (\$, H . . \$-S & \$ 6 ; .. * + W
)- ; 5 T# 7 6X#% &' # &
= %< 3
T % % . \$I + + . H . , D
H . (S . . , ((* \$) . . \$) -
* . 6 F! # ; T% 8 5
T ;

7 --\$!\$. * H * -D *\$\$ H . . . S4
))+. \$. . * ,
 * 6 F!#; T%#/ 2& / 3
 T 7 # 7 7
 -- I -- . H++\$D++) H . . \$-S7\$-- ++\$
 * Mb 0 :# #F T# 3
 H 3
 5 4 (3
 7 ,I+) H\$ D\$\$\$) H .
 .. S)
 *\$ ' 8# M 5 c # ' ; #
 7
 ' F
 . . \$ H*-D+ H . . *S4 . - .)
 *(F T3# W 73F# X 6F# 7
 () 6
 T 8 7 -, \$! . .) (H(+ +D(+
 H . . . S4 . . \$)
 *) & #X TW#7 68# B
 3
 " 3
 3 0 1
 W 7 .)I +H))-D)+
 H . . \$-S7(W7. ++. /
 ** 6 6#% ; T# F W 3 ' :
 " 1 F
 ..+I- H D (H . . S . * \$-)
 *+ c 7# 8 8# 8 X3& 6

' 3
 T 8 7 --\$!) (H \$+*D \$, \$ H
 . . S4 + . (0
 *, M W>#% T# B / W# 3
 3
 8 8 6 M
 . , I -)H)\$D* H . . *S4
 +
 *- 9 !# @# F U# 6 : M
 3 6 / " #
 T 6 7 8 . -I+ (+ H *-\$(D *-\$ H .
 . \$-S7-' 8.-)+ 7
 +. 2 ; # W 9# F @# 3
 3 3 D
 " 5 87 8 6
 . -I \$ H\$. *D\$. \$ H . . S , , . . *
 + / @# 2 @# 2 ; # B T3
 3 3
 0 D " 5 H
 # # 3
 87 8 6
 . -I (, H() ,D()) H . . S
 - +)*-
 + F W# 7 /#; @# !
 3 " 5 3
 7 7
 ! . I().H ((. H . . *S4 .
 ((