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A copper(II) metal–organic hydrogel as a heterogeneous reusable catalyst for the synthesis of 1,3-oxathiolane-2-thiones from the reaction of CS₂ and epoxides

Mahesh Samanta, Tapas Mahata and Manish Bhattacharjee  *

A copper(II) metalorganic hydrogel has been synthesised using the ligand ((2-hydroxynaphthalen-1-yl)methyl)-L-threonine and characterised. The hydrogel is an efficient, reusable catalyst for the selective synthesis of 1,3-oxathiolane-2-thiones from the reaction of CS₂ and epoxides under solvent-free conditions.

Metalorganic gels (MOGs) constructed from metal ions and organic ligands are of immense importance due to their promising application in different fields,¹ including catalysis.^{1c} Among the MOGs, metalhydrogels² are of current interest. These MOGs have potential as efficient catalysts due to their heterogeneous nature³ and recycling ability.⁴ The MOGs containing the first row transition metals as a catalyst are important because of their low-cost, non-toxic nature, and easy availability.

Carbon disulphide (CS₂) is an underutilised C₁ synthon for synthesising sulphur-containing heterocycles. Carbon disulphide, having a low boiling point, is produced in the manufacturing process of viscose fibres and cellophane films.⁵ When released into the environment, it is converted into COS and SO₂, which are major environmental pollutants.⁶

There are reports, including some from our laboratory,⁷ on the conversion of CO₂ to cyclic carbonates from the reaction of epoxides using homogeneous and heterogeneous catalysts. However, unlike CO₂, the reports on the catalytic conversion to thiocarbonates from the reaction of epoxide with CS₂ are not numerous.⁶

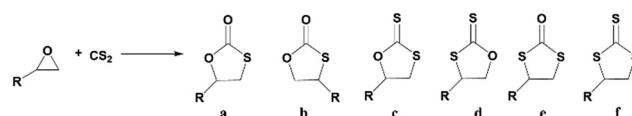
Heterocyclic and organosulfur compounds are important in the pharmaceutical, agrochemical, and other fields of chemistry. Heterocyclic compounds of sulphur, like cyclic dithiocarbonates, have a wide range of applications as building blocks for other organosulphur compounds and polymer synthesis. The synthesis of cyclic carbonates using CO₂ is highly selective. Nevertheless, in the reaction of CS₂ with epoxides, the selectivity of the products is a major issue. There are many different

products possible depending on the reaction conditions and the catalysts used (Scheme 1).

North and coworkers have reported an aluminium (salen) complex [Al(salen)]₂O catalysed reaction of epoxide with CS₂ in the presence of tetrabutylammonium bromide (TBAB). It has been reported that 1,3-oxathiolane-2-thiones and 1,3-dithiolane-2-thiones are produced depending on the reaction temperature.^{8a} The same group has reported a [Ti(salen)O]₂ catalysed reaction of epoxides with CS₂ in the presence of TBAB, which produces di- and/or trithiocarbonates.^{8b} In another report, it has been shown that lithium *tert*-butoxide, LiO^tBu, catalyses the reaction of epoxides with CS₂ regio- and stereoselectively.^{9a} A gallium aminotrisphenolate complex has also been shown to be an effective catalyst for the reaction of CS₂ with epoxides.^{9b}

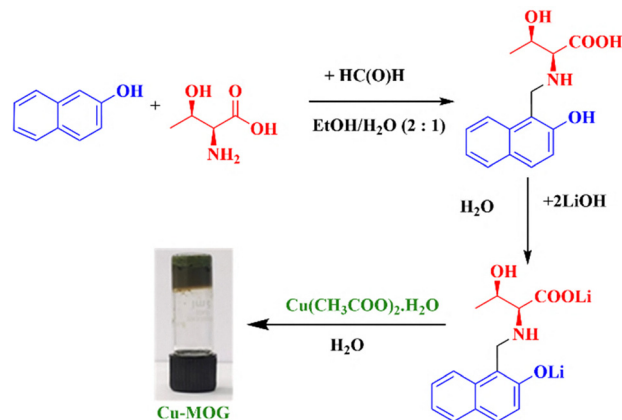
Heterogeneous catalysis has many more advantages over homogeneous catalysis due to the easy separation of the catalyst and reusability. To the best of our knowledge, except for one report on a hydrotalcite MG30 catalysed reaction,¹⁰ there is no report on a heterogeneous and reusable catalyst for the reaction of CS₂ with epoxide. It may also be noted that, unlike the synthesis of the metal complexes, the synthesis of MOGs does not involve a multistep synthesis and is straightforward. We recently embarked upon the synthesis and properties of metal–organic gels using low molecular weight gelators.¹¹ We have reported MOG-catalysed reactions of CO₂^{7a} and SO₂^{11c} with epoxides.

In continuation of our studies on MOG-catalysed reactions, we report herein the synthesis of a copper(II)-containing multiresponsive metalhydrogel using a new low molecular weight gelator, ((2-hydroxynaphthalen-1-yl)methyl)-L-threonine (Scheme 2), and its



Scheme 1 Possible products of the reaction between epoxides and CS₂.

Department of Chemistry Indian Institute of Technology, Kharagpur 721302, India.
E-mail: mxb@iitkgp.ac.in



Scheme 2 Synthesis of the gelator and the Cu-MOG.

properties and catalytic activity towards selective cycloaddition of CS_2 to epoxides.

The ligand ((2-hydroxynaphthalen-1-yl)methyl)-L-threonine was synthesised from the reaction of β -naphthol with L-threonine and formaldehyde in aqueous ethanol. The ligand was characterised by high-resolution mass spectrometry (HRMS), IR, and ^1H and ^{13}C NMR spectroscopy.

The HRMS (Fig. S1, SI) shows the molecular ion peak at $m/z = 276.1243$ corresponding to $\{\text{C}_{15}\text{H}_{18}\text{NO}_4 \{\text{M} + \text{H}^+\}\}$ [calculated mass = 276.1236]. The ^1H NMR spectrum (Fig. S2, SI) shows a doublet at 1.12 ppm (3H, d, $J = 6.2$ Hz) due to the $-\text{CH}_3$ protons of the threonine moiety. The signal for the $-\text{CH}$ protons of the $-\text{CHNH}$ group and $-\text{CH}_3\text{CH}(\text{OH})$ of threonine appear at 3.06 ppm (1H, d, $J = 7.7$ Hz) and at 3.71 ppm (1H, m), respectively. The signals for the aromatic protons of the naphthalene moiety appear at 6.96 ppm (1H, d, $J = 8.9$ Hz), 7.09 ppm (1H, m), 7.37 ppm (1H, m), 7.56 ppm (1H, d, $J = 8.8$ Hz), 7.65 ppm (1H, d, $J = 7.7$ Hz), and 7.81 ppm (1H, d, $J = 8.5$ Hz). The ^{13}C NMR spectrum (Fig. S3, SI) and IR spectrum (Fig. S4, SI) are in order.

Cu-MOG was prepared by mixing an aqueous solution of the dilithium salt of the ligand, Li_2HL (0.04 mmol in 0.5 mL H₂O), with an aqueous solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.04 mmol in 0.5 mL H₂O) in a glass vial at room temperature. The optimal metal-to-gelator stoichiometry was determined by varying the Cu^{2+} :gelator ratio. The minimum gelation concentration (MGC) was measured to be 18.99 mg mL^{-1} (1.899% w/v) (Fig. S5, SI).

The MALDI-TOF mass spectrum (Fig. S6, SI) of the Cu-MOG shows a prominent peak at $m/z = 391.531$, corresponding to $\{[\text{CuL}(\text{H}_2\text{O})_3] + \text{H}^+\}$ {calculated mass for $\text{C}_{15}\text{H}_{23}\text{NO}_4\text{Cu} = 392.077$ } along with other peaks. Thus, it is clear that the ligand forms a 1:1 complex.

A comparison of the IR spectrum of the free ligand with that of the gel clearly shows that the ligand is coordinated to the copper centre, as evidenced by the marked shift of the $\text{C}=\text{O}$ stretching frequency of the ligand (Fig. S7, SI).

The survey scan of the X-ray photoelectron spectroscopy (XPS) of the gel shows the presence of Cu 2p, N 1s, O 1s, and

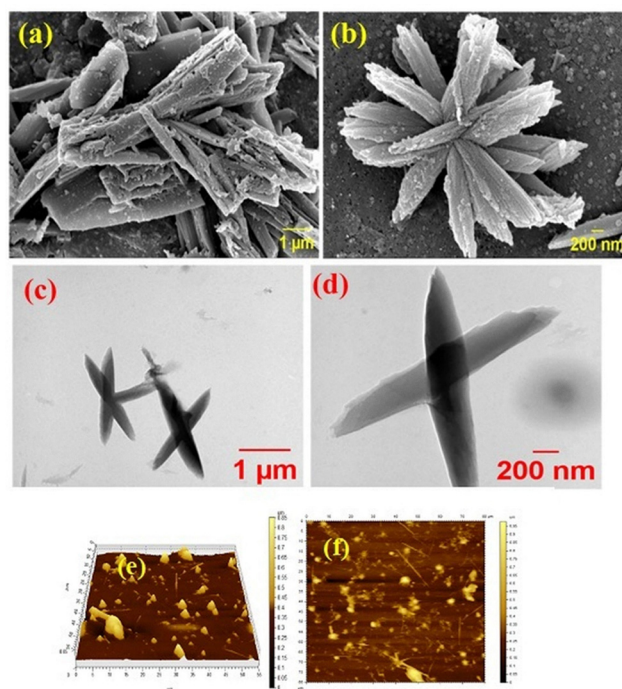


Fig. 1 FESEM (a) and (b), HRTEM (c) and (d) and AFM (e) and (f) images of the Cu-MOG.

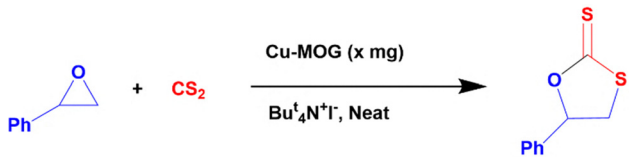
C 1s signals (Fig. S8, SI). The high-resolution Cu 2p spectrum (Fig. S9a, SI) reveals multiple deconvoluted peaks at 932.63 eV, 932.82 eV, and 934.28 eV, corresponding to the Cu $2p_{3/2}$ region, and at 952.32 eV, 952.52 eV, and 954.33 eV in the Cu $2p_{1/2}$ region. The low-binding-energy peaks (931.5–931.7 eV and 951.2–951.4 eV) are consistent with Cu^+ , while the higher-energy peaks at 934.28 eV and 954.33 eV are attributed to Cu^{2+} species.¹²

The powder X-ray diffraction (PXRD) pattern (Fig. S10, SI) exhibits a series of sharp and intense diffraction peaks, indicating a high degree of crystallinity.

The morphology of the Cu-MOG was examined by field emission scanning electron microscopy (FESEM), FESEM elemental analysis, high-resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM) (Fig. S11, SI). The FESEM images (Fig. 1a and b) show a well-defined rod-shaped petal morphology, indicative of a highly organised supramolecular architecture. Similarly, the HRTEM images (Fig. 1c and d) confirm the presence of these rod-shaped and petal-like assemblies. The AFM images (Fig. 1e and f) also corroborate the FESEM and HRTEM images.

The Cu-MOG shows chemoresponsive, mechanoresponsive, and pH-responsive behaviour (Fig. S12, SI).

The amplitude and frequency sweep tests were conducted to determine the mechanical strength and viscoelastic nature of the gel. The plot of G' and G'' against angular frequency (ω) reveals that the gap between G' and G'' was large for the entire region of frequency, and their frequency-invariant character shows the viscoelastic nature of the hydrogel (Fig. S13, SI). The results of the step-strain experiment clearly show the thixotropic behaviour and exceptional self-healing capability.

Table 1 Optimization of the cycloaddition of CS₂ with epoxides^a


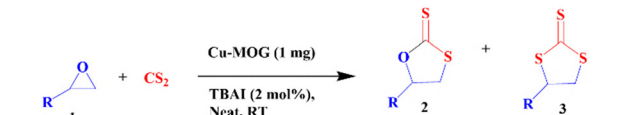
Entry	Cat. (mg)	TBAI (mol%)	Solvent	Time (h)	Temp. (°C)	Yield ^b (%)
1	Xerogel (2)	5	Neat	24	rt	87
2	Xerogel (3)	5	Neat	24	rt	90
3	Xerogel (4)	5	Neat	24	rt	81
4	Xerogel (5)	5	Neat	24	rt	85
5	Xerogel (1)	5	Neat	24	rt	89
6	Xerogel (1)	2	Neat	24	rt	96
7	Xerogel (1)	2	Neat	8	rt	99
8	Gel (1)	2	Neat	8	rt	61
9	—	2	Neat	8	rt	23
10	Xerogel (1)	—	Neat	8	rt	61
11	Xerogel (1)	2	H ₂ O ^c	8	rt	60

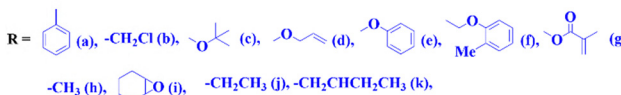
^a Styrene oxide **1a** (5.0 mmol), CS₂ **2a** (6.0 mmol), and Cu-MOG (× mg).^b Isolated yield. ^c H₂O (2 mL).

We optimised the cycloaddition using the model reaction of styrene oxide (**1a**) with CS₂ in the presence of tetrabutyl ammonium iodide (TBAI) as a co-catalyst and Cu-MOG as the catalyst. We tested the catalytic activity of Cu-MOG using both gel material and xerogel material without any solvent. Initially, 2 mg of the xerogel was used in the presence of 5 mol% of TBAI. After 24 hours, 5-phenyl-1,3-oxathiolane-2-thione (**2a**) was isolated in an 87% yield (Table 1, entry 1). We gradually varied the catalyst concentration from 1 mg to 5 mg in the presence of 5 mol% of TBAI (Table 1, entries 2 to 5), keeping the reaction time the same (24 hours). The yield of the product varies from 81% to 90%. The highest yield of the product was obtained when the reaction was carried out for 8 hours in the presence of 1.0 mg of the xerogel and 2 mol% of TBAI (entry 7, Table 1). In the presence of only TBAI (2 mol%), the product was obtained in a 23% yield in 8 hours (entry 9, Table 1). Similarly, when the reaction was carried out only in the presence of the xerogel, the yield of the product was found to be 61% in 8 hours (entry 10, Table 1). The reaction carried out in water as a solvent afforded the product in 60% yield (entry 11, Table 1).

We then explored the scope of the catalytic reaction under the optimised conditions. We have carried out the reactions between different epoxides and CS₂, and the corresponding products were isolated in excellent yields (Table 2). All the compounds have been characterised by ¹H and ¹³C NMR spectroscopy, and were found to be the same as those of the reported compounds and the compounds **2j**, **3j**, **2k**, and **3k** were characterised by mass spectrometry (Fig. S40–S45, SI).

In most of the cases (**1a** to **1g**), we obtained the corresponding oxathiolane-2-thione (**2**) as the exclusive product, selectively in excellent yields (entries 1 to 7, Table 2). However, in the cases of **1h** and **1i**, we obtained the corresponding 1,3-dithiolane-2-thione, **3h** and **3i**, respectively, in good to excellent yields (entries 8 and 9, Table 2). In the cases of **1j** and **1k**, we obtained the corresponding oxathiolane-2-thione and

Table 2 Scope of the Cu-MOG catalysed reaction of epoxides with CS₂^a


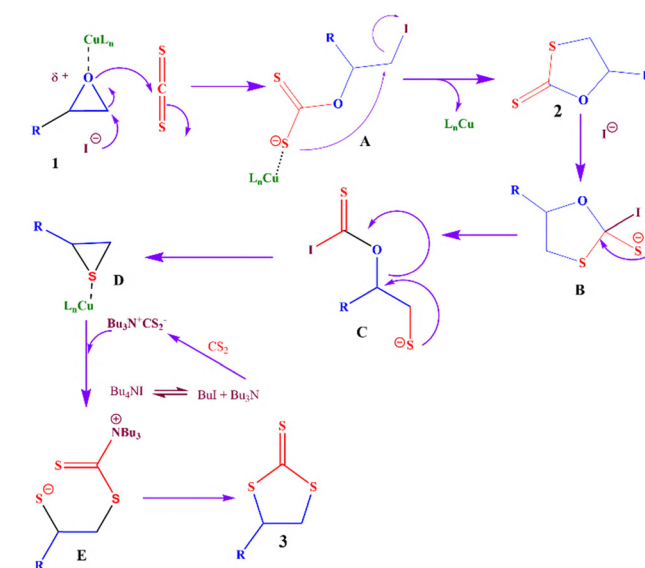
R = 

Entry	Substrate	Product	Selectivity (2 : 3)	Yield ^b (%)	TON
1	1a	2a	100 : 0	99	1941
2	1b	2b	100 : 0	96	1882
3	1c	2c	100 : 0	98	1921
4	1d	2d	100 : 0	86	1686
5	1e	2e	100 : 0	99	1941
6	1f	2f	100 : 0	99	1941
7	1g	2g	100 : 0	97	1902
8	1h ^c	3h	0 : 100	60	1176
9	1i ^c	3i	0 : 100	91	1784
10	1j ^c	2j, 3j	63 : 37	91	1784
11	1k ^c	2k, 3k	75 : 25	97	1902

^a Epoxide **1** (5.0 mmol), CS₂ (6.0 mmol) and Cu-MOG {1.0 mg; 2.55 × 10⁻⁶ mol, of [CuL(H₂O)₃]}, TBAI (2 mol%) at room temperature.^b Isolated yield. ^c CS₂ (9 mmol).

dithiolane-2-thione in excellent yields with low selectivity (entries 10 and 11, Table 2). It has been proposed that the formation of thiirane **D** (Scheme 3) from the intermediate **C** proceeds by an S_N¹-type mechanism.^{8a} So, the relative stabilities of the carbocations may be responsible for the difference in the selectivity.

A comparison of the activity of Cu-MOG with those of the reported catalysts is given in Table S1 (SI), and it shows that, compared to the reported catalysts, the activity and selectivity of the Cu-MOG are higher.



Scheme 3 Plausible mechanism for the reduction and oxidation of the Cu(II) centre.

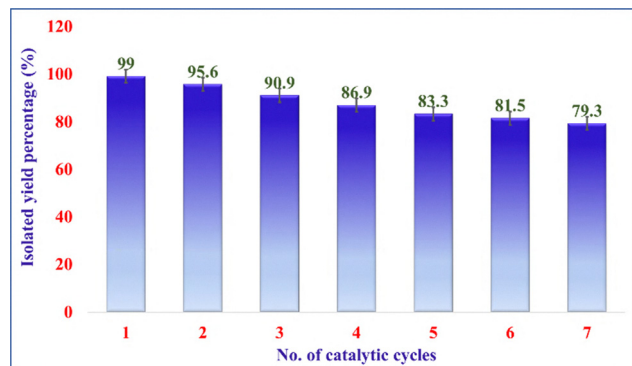


Fig. 2 Recyclability study of the Cu-MOG for five cycles.

We have also studied the reaction profile using gas chromatography (GC). It was observed that the initial rate of the reaction is slightly slow. After 2 hours, the rate increases gradually (Fig. S14; SI).

We examined the reusability of the catalyst in the reaction of **1a** with CS₂. After the reaction, ethyl acetate was added, and the Cu-MOG was recovered by centrifugation. The xerogel was washed with acetone, water, and diethyl ether, and dried at 50 °C. The xerogel was used up to the seventh cycle. During the seven catalytic cycles (Fig. 2), the catalytic efficiency of the Cu-MOG decreases. The yield of the product decreases from 99% to 79.3%. The decrease in the activity of the catalyst is due to the partial loss of the amount of catalyst during the recovery of the xerogel by centrifugation.

We examined the integrity of the Cu-MOG xerogel after the first cycle of the catalytic reaction between **1a** and CS₂ by recording the FESEM images and FESEM elemental analysis, PXRD and IR spectrum of the xerogel. From the FESEM images and elemental analysis (Fig. S15, SI), PXRD data and IR spectrum (Fig. S16, SI), we can conclude that the integrity of the Cu-MOG remains unaltered after the catalytic reaction.

We have checked the extent of leaching of the catalyst by GC monitoring of the reaction between **1a** and CS₂. The xerogel was filtered after 4 hours, and the reaction was continued for 8 hours. After the filtration of the catalyst, we could not detect any product formation (Fig. S17, SI). Thus, it is clear that the extent of catalyst leaching is negligible.

The proposed mechanism of the reaction is shown in Scheme 3. The plausible mechanism has been proposed based on the reported reaction mechanism catalysed by [Al(salen)]₂O.^{8a}

In conclusion, we have synthesised a new multiresponsive Cu-MOG using the ligand, ((2-hydroxynaphthalen-1-yl)methyl)-L-threonine. The MOG is an efficient, heterogeneous, and reusable catalyst for the highly selective synthesis of oxathiolane-2-thiones from the reaction of epoxides with CS₂. In the case of 2-methyl oxirane and cyclohexane oxide, the corresponding 1,3-dithiolane-2-thiones were obtained exclusively.

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Conflicts of interest

There are no conflicts to declare.

Data availability

All data supporting this study are included in the article and its SI (experimental procedures, spectral data, table, spectra and figures). See DOI: <https://doi.org/10.1039/d5cc03856a>

Notes and references

- (a) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278–281; (b) Z. Xie, L. Ma, K. E. deKrafft, A. Jin and W. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 922–923; (c) M. Martinez-Calvo, O. Kotova, M. E. Mobius, A. P. Bell, T. McCabe, J. J. Boland and T. Gunnlaugsson, *J. Am. Chem. Soc.*, 2015, **137**, 1983–1992; (d) X. M. Li, J. Y. Li, Y. A. Gao, Y. Kuang, J. F. Shi and B. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 17707–17709; (e) J. F. Miravet and B. Escuder, *Chem. Commun.*, 2005, 5796–5798; (f) P. Sutar and T. K. Maji, *Chem. Commun.*, 2016, **52**, 8055–8074.
- (a) S. Saha, J. Bachl, T. Kundu, D. D. Diaz and R. Banerjee, *Chem. Commun.*, 2014, **50**, 3004–3006; (b) S. Basak, J. Nanda and A. Banerjee, *Chem. Commun.*, 2014, **50**, 2356–2359.
- (a) P. Li, S. Regati, H. Huang, H. D. Arman, J. C. G. Zhao and B. Chen, *Inorg. Chem. Front.*, 2015, **2**, 42–46; (b) X. Kang, J. Zhang, W. Shang, T. Wu, P. Zhang, B. Han, Z. Wu, G. Mo and X. Xing, *J. Am. Chem. Soc.*, 2014, **136**, 3768–3771; (c) L. Duran Pachon, van J. H. Maarseveen and G. Rotheberg, *Adv. Synth. Catal.*, 2005, **347**, 811–815; (d) M. Nasr-Esfahani, I. Mohammadpour-Baltork, A. R. Khosropour, M. Moghadam, V. Mirkhani, S. Tangestaninejad and H. Amiri Rudbari, *J. Org. Chem.*, 2014, **79**, 1437–1443.
- (a) Y. He, Z. Bian, C. Kang, Y. Cheng and L. Gao, *Chem. Commun.*, 2010, **46**, 3532–3534; (b) B. Dervaux and Du. F. E. Prez, *Chem. Sci.*, 2012, **3**, 959–966.
- D. Majumdar, A. Bhanarkar, C. Rao and D. Douda, *Atmospheric Environ.: X*, 2022, **13**, 100157.
- C. Diez-Poza, L. Álvarez-Miguel, M. E. G. Mosquera and C. J. Whiteoak, *Org. Biomol. Chem.*, 2023, **21**, 3733–3755.
- (a) C. K. Karan, M. C. Sau and M. Bhattacharjee, *Chem. Commun.*, 2017, **53**, 1526–1529; (b) K. K. Pradhan, A. Sahaw and M. Bhattacharjee, *Langmuir*, 2025, **41**, 20954–20966; (c) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou and W.-Q. Deng, *Nat. Commun.*, 2013, **4**, 1960; P.-Z. Li, X.-J. Wang, J. Liu, J. S. Lim, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 2142–2145; (d) S. Bhunia, R. A. Molla, V. Kumari, S. M. Islamb and A. Bhaumik, *Chem. Commun.*, 2015, **51**, 15732–15735.
- (a) W. Clegg, R. W. Harrington, M. North and P. Villuendas, *J. Org. Chem.*, 2010, **75**, 6201–6207; (b) C. Beattie and M. North, *ChemCatChem*, 2014, **6**, 1252–1259.
- (a) J. Diebler, A. Spannenberg and T. Werner, *Org. Biomol. Chem.*, 2016, **14**, 7480–7489; (b) L. Álvarez-Miguel, M. E. G. Mosquera and C. J. Whiteoak, *Org. Biomol. Chem.*, 2022, **20**, 9629–9638.
- R. Maggi, C. Malmassari, C. Oro, R. Pela, G. Sartori and L. Soldi, *Synthesis*, 2008, 53–56.
- (a) C. K. Karan and M. Bhattacharjee, *ACS Appl. Mater. Interfaces*, 2016, **8**, 5526–5535; (b) M. Dutta, S. Ghora, A. Sahaw, C. Raj and M. Bhattacharjee, *Langmuir*, 2025, **41**, 1960–19613; (c) C. K. Karan and M. Bhattacharjee, *Eur. J. Inorg. Chem.*, 2019, 3605–3611; (d) C. K. Karan, S. Mallick, C. R. Raj and M. Bhattacharjee, *Chem. – Eur. J.*, 2019, **25**, 14775–14779.
- T. M. Ivanova, K. I. Maslakov, A. A. Sidorov, M. A. Kiskin, R. V. Linko, S. V. Savilov, V. V. Luninb and I. L. Eremenko, *J. Electron Spectrosc. Relat. Phenom.*, 2020, **238**, 146878.