



Supramolecular Subphthalocyanine Cage as Catalytic Container for the Functionalization of Fullerenes in Water

Ainhoa Salazar, Marta Moreno-Simoni⁺, Sunit Kumar⁺, Jorge Labella, Tomás Torres,* and Gema de la Torre*

Abstract: Herein we report the first example of a supramolecular cage that works as a catalytic molecular reactor to perform transformations over fullerenes in aqueous medium. Taking advantage of the ability of metallo-organic Pd(II)-subphthalocyanine (SubPc) capsules to form stable host:guest complexes with C₆₀, we have prepared a water-soluble cage that provides a hydrophobic environment for conducting cycloadditions over encapsulated C₆₀, namely, Diels–Alder reactions with anthracene. Indeed, the presence of catalytic amounts of SubPc cage dissolved in water promotes co-encapsulation of insoluble C₆₀ and anthracene substrates, allowing the reaction to occur inside the cavity under mild conditions. The lower stability of the host: guest complex with the resulting C₆₀ cycloadduct facilitates its displacement by pristine C₆₀, which grants catalytic turnover. Moreover, bis-addition compounds are regioselectively formed inside the cage when using excess anthracene.

Inspired by natural enzymes, many researchers have pursued the development of catalysts that emulate the capabilities of reactive cavities in biological systems.^[1] Supramolecular hosts,^[2] and in particular coordination

cages,^[3] have drawn considerable attention as artificial catalysts for mimicking the reactivity of enzymes, since they are dynamic species that can reversibly encapsulate substrate molecules. Interestingly, several organic transformations have shown a sharp increase in the reaction rate when they are performed in the cavities of self-assembled coordination nanocages.^[4–7] Some of them have been carried out in water-soluble molecular hosts that afford encapsulation of insoluble substrates.^[8–14] However, in most of the systems, product inhibition prevents the cage from showing a true catalytic behavior, which results in the requirement of stoichiometric quantities of the host. Only a limited number of examples utilize pure catalytic conditions.^[15–19] In particular, there are several reports that describe a significant acceleration of Diels–Alder reactions in the cavities of synthetic pockets,^[12–14] but strong complexation of the cycloaddition product within the cage results in product inhibition and thereby prevents catalytic turnover. Therefore, promoting product release from the cage is still a non-fully resolved issue.

Over the last years, the use of metallo-organic cages to perform chemical transformations over C₆₀ has become a hot topic since these compounds are key components in state-of-the-art technologies, such as molecular electronics and photovoltaics.^[20] The space confinement in the host: guest complexes impacts the reactivity of C₆₀, allowing to undertake addition reactions under mild conditions (Scheme 1).^[21–27] The cages have been also utilized as supramolecular masks, providing an excellent control on the regioselectivity of multi-addition reactions over encapsulated C₆₀.^[23–27] In all these examples, the reactions take place in organic solvents and, crucially, they require stoichiometric amounts of the cage, only showing a true catalytic behavior by implementing complex phase transfer protocols.^[25] On this basis, the development of cage-catalyzed reactions over C₆₀ in aqueous media would imply a significant step further in the field.

Most of the coordination cages utilized as nanocontainers for organic transformations over C₆₀ are built with porphyrins, because of their extended aromatic surface. Also, metallo-supramolecular cages built with phthalocyanine derivatives^[28] readily form host:guest complexes with fullerenes, which are particularly stable in the case of subphthalocyanine (SubPc) capsules (Scheme 1)^[29] due to the shape complementarity between the concave face of the bowl-shaped SubPc and the spherical π -surface of C₆₀.^[30,31] In spite of these precedents, the use of SubPc-based nanocontainers for the functionalization of C₆₀ has been briefly explored. In this line, taking advantage of the SubPc ability

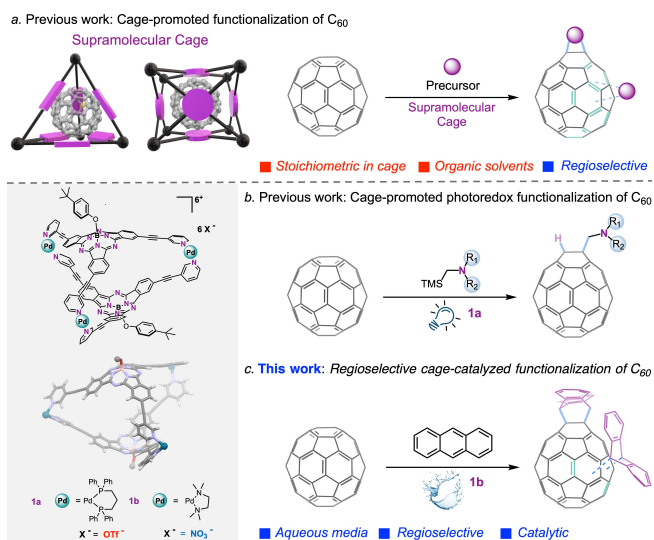
[*] A. Salazar, Dr. M. Moreno-Simoni,⁺ Dr. S. Kumar,⁺ J. Labella, Prof. T. Torres, Prof. G. de la Torre
 Department of Organic Chemistry, Universidad Autónoma de Madrid
 Campus de Cantoblanco C/Francisco Tomás y Valiente 7, 28049 Madrid (Spain)
 E-mail: tomas.torres@uam.es
 gema.delatorre@uam.es

Prof. T. Torres, Prof. G. de la Torre
 Institute for Advanced Research in Chemical Sciences (IAdChem),
 Universidad Autónoma de Madrid
 Campus de Cantoblanco, 28049 Madrid (Spain)

Prof. T. Torres
 Instituto Madrileño de Estudios Avanzados (IMDEA),
 Campus de Cantoblanco, 28049 Madrid (Spain)

[⁺] These authors contributed equally to this work.

© 2023 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.



Scheme 1. Cage-promoted transformations of fullerenes.

to trigger photoinduced electron transfer processes after excitation with visible light,^[32] our group has recently reported unprecedented, green-light induced photoredox addition reactions over C_{60} encapsulated in a dimeric Pd(II)–SubPc cage (Scheme 1).^[33]

Going one step further, we describe here a water-soluble analog of this SubPc cage that performs as a hydrophobic, fully catalytic confined microenvironment to realize Diels–Alder cycloaddition reactions over encapsulated C_{60} dienophile in an eco-friendly aqueous media under mild conditions. Specifically, we have selected the well-known Diels–Alder cycloaddition with anthracene.^[34] Although the thermal stability of the adduct formed with C_{60} fullerene (C_{60} –Ant) is low due to retro-Diels Alder events, we considered this reaction an appropriate model since the rigidity and bulkiness of the resulting fullerene adduct could destabilize the resulting host:guest complex, facilitating displacement of the adduct by pristine C_{60} and thereby allowing catalytic turnover. It is also demonstrated that both space-confinement and cavity-promoted co-encapsulation of the reactants are key aspects for the success of the reaction, that otherwise would not occur in this medium.

As mentioned above, the SubPc₂Pd₃ capsule **1a** (Scheme 1) formed by self-assembly of C₃ symmetry tris(3-pyridylethynyl)SubPc with 1,3-bis(diphenylphosphino)propane ditriflate palladium(II), forms stable 1:1 host–guest complexes with C_{60} and C_{70} fullerenes, with binding constants as large as $5 \times 10^5 \text{ M}^{-1}$.^[29,33] In the present work we have prepared a water-soluble form of this cage, using the same SubPc building block but assembled with (*N,N,N',N'*-tetramethylethylenediamine)dinitrate palladium(II) (See Supporting Information). The resulting hexacationic SubPc₂Pd₃ capsule **1b** (Scheme 1) counterbalanced by nitrate anions proved soluble in water when injected from DMSO to reach H₂O/1 % DMSO solutions of up to 1.0 mM concentration.

The progress of the cavity-promoted Diels Alder reaction between anthracene and C_{60} was monitored by ¹H

NMR spectroscopy. Initially, the reaction was performed with 0.2 equivalents of **1b** in D₂O/DMSO (1 %) at 50 °C (Table 1, entry 1). The reaction was heated for three days, but only ¹H NMR signals corresponding to the cage and the starting anthracene could be observed. However, when temperature was increased to 80 °C (Table 1, entry 2), a new signal at 5.84 ppm appeared, corresponding to Csp³–H atom of the C_{60} adduct C_{60} –Ant. The progress of the reaction was monitored for 3 days, which led to 40 % conversion (Figure 1). Either longer reaction times (Supporting Information) or temperature increase up to 100 °C (Table 1, entry 3) derived in evident decomposition of the cage. Aiming at improving the catalytic turnover, the ratio of **1b** was reduced to 10 % and, indeed, the conversion raised to 46 % (Table 1, entry 4). To our delight, when the reaction was carried out

Table 1: Optimization of the Diels–Alder reaction of C_{60} with anthracene catalyzed by **1b** in D₂O/DMSO-*d*₆ mixtures.^[a]

Entry	Anthracene [equiv]	1b [equiv]	DMSO- <i>d</i> ₆ content [%]	T [°C]	Conversion [%]
1	1	0.2	1	50	–
2	1	0.2	1	80	40
3	1	0.2	1	100	–
4	1	0.1	1	80	46
5	1	1.0	10	80	13

[a] Reaction conditions: C_{60} (0.004 mmol), **1b** (1 mM).

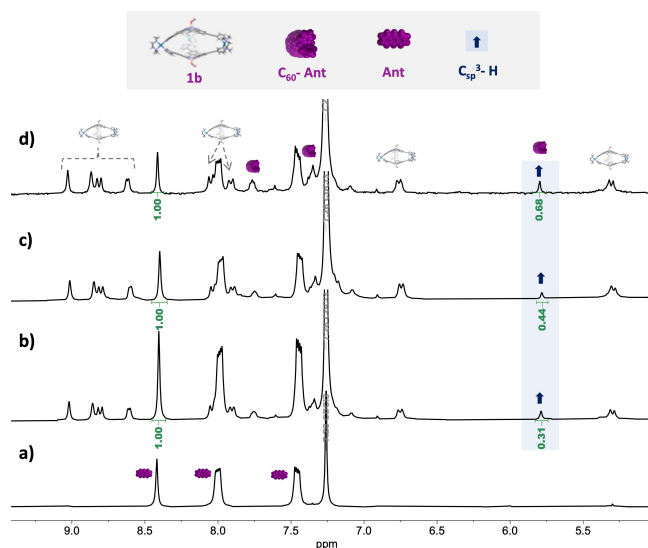


Figure 1. ¹H NMR monitoring (300 MHz, rt) of the progress of the Diels–Alder reaction between C_{60} and anthracene in aqueous solution of cage **1b**. The spectra were registered after solvent removal at rt and addition of CDCl₃:CS₂ over measured aliquots. [a] Before, and after the reaction at 80 °C for [b] 1 day, 23 %; [c] 2 days, 31 %; [d] 3 days, 40 % conversion.

with stoichiometric quantities of **1b** (Table 1, entry 5), it proceeded with lower conversion yield (i.e., 13 %), confirming that catalytic conditions are beneficial in terms of both efficiency and atom economy. A possible rationale for this finding is that co-encapsulation of the substrate molecules in the cavity of the SubPc capsule is statistically disfavored when using it in stoichiometric amounts.

Once the catalytic ability of **1b** was proved and conditions for the Diels–Alder reaction optimized, we turned to determine the potential of **1b** as a supramolecular template to promote multi-cycloadditions of anthracene to fullerene. As the aromatic scaffold of the capsule masks a significant part of the C₆₀ surface, it is expected that bis- or even tris-addition could take place regioselectively over the unshielded double bonds. Although a lower stability of C₆₀–Ant in the capsule cavity is demonstrated by the event of catalytic turnover and by theoretical calculations (see below), multi-additions could take place simultaneously at different double bonds of the fullerene before the reaction product is released from the cavity and replaced by pristine fullerene.

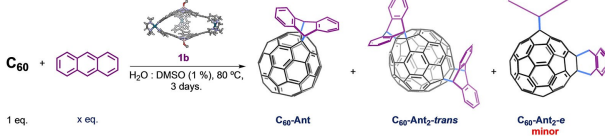
Several reactions were set using 0.1 eq. of **1b** and increasing amounts of anthracene, from 1 to 25 equivalents. Crudes were first analyzed by HPLC, which showed a broad peak with larger retention times than that of C₆₀–Ant that progressively increased in intensity along with the use of larger amounts of anthracene (Supporting Information). Next, we turned to ¹H NMR identification of the resulting products. To assess the conversion into the different addition compounds, reaction crudes were rapidly passed through a silica plug to isolate the mixture of fullerenes, which was then analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard to determine the ratio of each compound (Table 2). As the ¹H NMR pattern for bisaddition adducts with fullerene had been previously reported in the literature,^[33] we could identify the *trans*-3 bisadduct (C₆₀–Ant₂–*trans*) as the more abundant resulting from a regioselective multiaddition process, which is consistent with theoretical calculations (see below). Using 5 equivalents of anthracene (Table 2, entry 1), 39 % and

31 % yields were calculated for C₆₀–Ant and C₆₀–Ant₂–*trans*, respectively, with regard to starting C₆₀, while optimal 46 % and 40 % yields were obtained when using 10 equivalents of anthracene (entries 2 and 3). However, larger amounts of anthracene caused a notable decrease in mono- and bis-adduct conversion, probably as a consequence of the impeded encapsulation of fullerene in the presence of such amounts of anthracene. It should be noted that, after purification of the mixture by preparative TLC, we could also detect a minor amount of the equatorial bisadduct (C₆₀–Ant₂–*e*) (see Supporting Information), which formation is also supported by theoretical calculations. However, the formation of tris-adducts was not detected, neither by NMR analysis, nor by TLC.

To further confirm the catalytic abilities of **1b** in the synthesis of mono- and bisadducts in aqueous media, we prepared and characterized (Supporting Information) a **1b**⊂C₆₀ host:guest complex and performed the Diels–Alder reaction using 10 eq. of anthracene (entry 6), which, remarkably, rendered good but lower yields in both C₆₀–Ant and C₆₀–Ant₂–*trans*. Eventually, a reaction was set using C₆₀–Ant₂–*trans* as starting material in an attempt to obtain a C₆₀–Ant₃ derivative, but no traces of any type of tris-adduct were observed.

To shed light into the origin of these findings, theoretical calculations at the GFN2-xTB level were performed.^[35] The optimized structures of **1b**, as well as its complex with C₆₀, C₆₀–Ant, C₆₀–Ant₂–*trans* and C₆₀–Ant₂–*e* are depicted in Figure 2. Interestingly, it was found that the cavity size of the SubPc cage varies with C₆₀ complexation. Thus, the cage experiences an axial elongation (d_{bowl–bowl}) of about 2.8 Å, as well as an equatorial contraction (d_{Pd–Pd}) of about 1.9 Å. This distortion mainly arises from conformational changes in the peripheral Pd-alkynylpyridine complex, rather than from variations in the bowl-depth of SubPcs. It should be noted that the distortion is less pronounced in the case of C₆₀–Ant, C₆₀–Ant₂–*trans* and C₆₀–Ant₂–*e* host:guest complexes. We attributed this finding to the steric hindrance provided by the anthracene units, which force the fullerene to shift from the cage axis, thereby leading to a cavity compression for maximizing the non-covalent interactions (Figure 2). With the aim of understanding how the addition reaction takes place, the pre-reactive complex between C₆₀ and anthracene was optimized (Figure 2c). Remarkably, the anthracene molecule tends to locate at the hydrophobic pocket formed by the *N,N,N',N'*-tetramethylethylenediamine ligands (Figure 2f). Based on this finding, we propose that these pockets serve as anthracene reservoirs which can react with the encapsulated fullerene. This assumption is in line with the fact that the reaction yield is lower when using stoichiometric amounts of **1b**, as the lower the concentration of the cage, the higher is the probability of co-hosting an anthracene unit and therefore the reaction with C₆₀. The resulting mono-adduct can then rotate and further react with another anthracene unit, leading to either C₆₀–Ant₂–*trans* or C₆₀–Ant₂–*e*. Insights into the binding affinity of the different complexes were then obtained by calculating the relative stabilization energy of the complexation of C₆₀, C₆₀–Ant₂–*trans* and C₆₀–Ant₂–*e*. As shown in Figure 2, the stabilization

Table 2: Conditions applied for the preparation of anthracene C₆₀-bisadducts in H₂O/DMSO 1 % mixtures in the presence of **1b**.^[a]



Entry	Anthracene [equiv]	1b [equiv]	C ₆₀ –Ant	Yield [%] C ₆₀ –Ant ₂ – <i>trans</i>
1	1	0.1	16	1
2	5	0.1	39	31
3	10	0.1	46	40
4	15	0.1	23	14
5	20	0.1	10	2
6 ^[b]	10	1	28	7

[a] Reaction conditions: C₆₀ (0.004 mmol), **1b** (1 mM). [b] Performed over **1b**⊂C₆₀ host:guest complex.

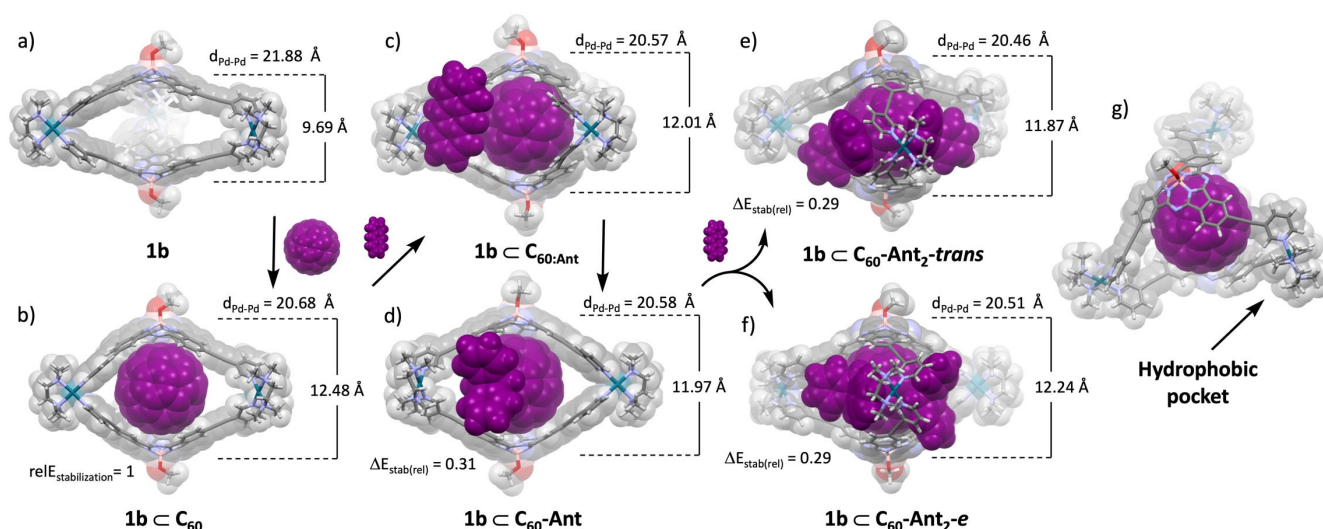


Figure 2. Minimum-energy structures of a) **1b**, b) **1b** ⊂ C_{60} , c) **1b** ⊂ C_{60} :anthracene, d) **1b** ⊂ C_{60} -Ant, e) **1b** ⊂ C_{60} -Ant₂-trans, and f) **1b** ⊂ C_{60} -Ant₂-e, calculated at the GFN2-xTB level. Relative stabilization energies, $d_{\text{bowl-bowl}}$ and $d_{\text{Pd-Pd}}$, are indicated in each case. g) Diagonal perspective of the minimum-energy structure of **1b** ⊂ C_{60} , indicating one of their three hydrophobic pockets.

is more than three times larger for C_{60} , compared to that of C_{60} -Ant, C_{60} -Ant₂-trans and C_{60} -Ant₂-e, probably due to the above-commented steric congestion. Moreover, it should be noted that these calculations only account for enthalpic factors, but the entropic term is expected to become important since the mono- and bis-adduct present a limited mobility within the cage. Based on these results, we can conclude that the SubPc cage is more prone to bind C_{60} than either mono- or bis-adducts, which is in line with the catalytic behavior experimentally observed. Importantly, **1b** ⊂ C_{60} -Ant₂-trans and **1b** ⊂ C_{60} -Ant₂-e present similar energies, suggesting that the higher formation of C_{60} -Ant₂-trans stems from a combination of the intrinsic reactivity of C_{60} and the kinetic pathway dictated by the cage.

In summary, water-soluble SubPc capsule **1b** has demonstrated an outstanding performance as hydrophobic nano-reactor to accelerate the Diels-Alder reaction between C_{60} and anthracene in water media, which, indeed, do not occur in the absence of cage. Importantly, **1b** can be used in catalytic amounts since i) it favors the co-encapsulation of substrates within the cavity; and ii) effortless departure from the cage of the resulting fullerene adducts takes place due to the lower stability of the corresponding host-guest complex, which enables catalytic turnover. As demonstrated by theoretical calculations, **1b** present three hydrophobic pockets surrounding the main cavity, which act as anthracene reservoirs and direct the cycloaddition. The capsule also provides an optimal space for the regioselective formation of a *trans*-3 bisadduct (C_{60} -Ant₂-trans).

All in all, we can conclude that SubPc cages are unique catalytic containers for the functionalization of fullerenes in water. Current efforts towards the development of other cage-catalyzed reactions are ongoing.

Acknowledgements

Financial support from the Spanish MCIN/AEI/10.13039/501100011033 (PID2020-116490GB-I00, PID2020-115801RB-C21, TED2021-131255B-C43), the Comunidad de Madrid and the Spanish State through the Recovery, Transformation and Resilience Plan ["Materiales Disruptivos Bidimensionales (2D)" (MAD2D-CM) (UAM1)-MRR Materiales Avanzados], and the European Union through the Next Generation EU funds is acknowledged. IMDEA Nanociencia acknowledges support from the "Severo Ochoa" Programme for Centres of Excellence in R&D (MINECO, Grant SEV2016-0686). S.K. acknowledges MSCA grant (101028059), and J.L. acknowledges MECD, Spain, for a F.P.U. fellowship. We acknowledge the generous allocation of computer time at the Centro de Computación Científica at the Universidad Autónoma de Madrid (CCC-UAM).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Catalysis • Fullerene • Metallosupramolecular • Subphthalocyanine • Water

[1] M. Dürrenberger, T. Heinisch, Y. M. Wilson, T. Rossel, E. Nogueira, L. Knörr, A. Mutschler, K. Kersten, M. J. Zimbron,

- J. Pierron, T. Schirmer, T. R. Ward, *Angew. Chem. Int. Ed.* **2011**, *50*, 3026–3029.
- [2] a) D. M. Vriezema, M. Comellas Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445–1490; b) M. Raynal, P. Ballester, A. Vidal-Ferran, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2014**, *43*, 1734–1787.
- [3] a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; b) C. J. Brown, F. D. Toste, R. G. Bergman, K. N. Raymond, *Chem. Rev.* **2015**, *115*, 3012–3035; c) Y. Xue, X. Hang, J. Ding, B. Li, R. Zhu, H. Pang, Q. Xu, *Coord. Chem. Rev.* **2021**, *430*, 213656.
- [4] J. Jiao, C. Tan, Z. Li, Y. Liu, X. Han, Y. Cui, *J. Am. Chem. Soc.* **2018**, *140*, 2251–2259.
- [5] S. Gonell, X. Caumes, N. Orth, I. Ivanović-Burmazović, J. N. H. Reek, *Chem. Sci.* **2019**, *10*, 1316–1321.
- [6] C. García-Simón, R. Gramage-Doria, S. Raoufmoghaddam, T. Parella, M. Costas, X. Ribas, J. N. H. Reek, *J. Am. Chem. Soc.* **2015**, *137*, 2680–2687.
- [7] S. S. Nurttila, W. Brenner, J. Mosquera, K. M. van Vliet, J. R. Nitschke, J. N. H. Reek, *Chem. Eur. J.* **2019**, *25*, 609–620.
- [8] T. Murase, Y. Nishijima, M. Fujita, *J. Am. Chem. Soc.* **2012**, *134*, 162–164.
- [9] V. M. Dong, D. Fiedler, B. Carl, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 14464–14465.
- [10] M. Yoshizawa, Y. Takeyama, T. Okano, M. Fujita, *J. Am. Chem. Soc.* **2003**, *125*, 3243–3247.
- [11] W. Cullen, M. C. Misuraca, C. A. Hunter, N. H. Williams, M. D. Ward, *Nat. Chem.* **2016**, *8*, 231–236.
- [12] M. Yoshizawa, M. Tamura, M. Fujita, *Science* **2006**, *312*, 251–254.
- [13] J. Kang, J. Rebek, *Nature* **1997**, *385*, 50–52.
- [14] Y. Nishioka, T. Yamaguchi, M. Yoshizawa, M. Fujita, *J. Am. Chem. Soc.* **2007**, *129*, 7000–7001.
- [15] D. Fiedler, H. van Halbeek, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 10240–10252.
- [16] P. Howlader, P. Das, E. Zangrando, P. S. Mukherjee, *J. Am. Chem. Soc.* **2016**, *138*, 1668–1676.
- [17] D. Samanta, S. Mukherjee, Y. P. Patil, P. S. Mukherjee, *Chem. Eur. J.* **2012**, *18*, 12322–12329.
- [18] W. Cullen, A. J. Metherell, A. B. Wragg, C. G. P. Taylor, N. H. Williams, M. D. Ward, *J. Am. Chem. Soc.* **2018**, *140*, 2821–2828.
- [19] I. Ahmad Bhat, A. Devaraj, P. Howlader, K.-W. Chi, P. S. Mukherjee, *Chem. Commun.* **2018**, *54*, 4814–4817.
- [20] G. de la Torre, G. Bottari, T. Torres, *Adv. Energy Mater.* **2017**, *7*, 1601700.
- [21] W. Brenner, T. K. Ronson, J. R. Nitschke, *J. Am. Chem. Soc.* **2017**, *139*, 75–78.
- [22] B. Chen, J. J. Holstein, S. Horiuchi, W. G. Hiller, G. H. Clever, *J. Am. Chem. Soc.* **2019**, *141*, 8907–8913.
- [23] M. Pujals, T. Pèlachs, C. Fuertes-Espinosa, T. Parella, M. García-Borràs, X. Ribas, *Cell Rep.* **2022**, *3*, 100992.
- [24] Z. Lu, T. K. Ronson, A. W. Heard, S. Feldmann, N. Vanthuyne, A. Martínez, J. R. Nitschke, *Nat. Chem.* **2023**, *15*, 405–412.
- [25] C. Fuertes-Espinosa, C. García-Simón, M. Pujals, M. García-Borràs, L. Gómez, T. Parella, J. Juanhuix, I. Imaz, D. Maspoch, M. Costas, X. Ribas, *Chem* **2020**, *6*, 169–186.
- [26] E. Ubasart, O. Borodin, C. Fuertes-Espinosa, Y. Xu, C. García-Simón, L. Gómez, J. Juanhuix, F. Gándara, I. Imaz, D. Maspoch, M. von Delius, X. Ribas, *Nat. Chem.* **2021**, *13*, 420–427.
- [27] V. Leonhardt, S. Fimmel, A.-M. Krause, F. Beuerle, *Chem. Sci.* **2020**, *11*, 8409–8415.
- [28] E. Fazio, C. J. E. Haynes, G. de la Torre, J. R. Nitschke, T. Torres, *Chem. Commun.* **2018**, *54*, 2651–2654.
- [29] I. Sánchez-Molina, B. Grimm, R. M. Krick Calderon, C. G. Claessens, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2013**, *135*, 10503–10511.
- [30] G. Lavarda, J. Labella, M. V. Martínez-Díaz, M. S. Rodríguez-Morgade, A. Osuka, T. Torres, *Chem. Soc. Rev.* **2022**, *51*, 9482–9619.
- [31] G. Zango, M. Krug, S. Krishna, V. Mariñas, T. Clark, M. V. Martínez-Díaz, D. M. Guldi, T. Torres, *Chem. Sci.* **2020**, *11*, 3448–3459.
- [32] G. Bottari, G. de la Torre, D. M. Guldi, T. Torres, *Coord. Chem. Rev.* **2021**, *428*, 213605.
- [33] M. Moreno-Simoni, T. Torres, G. de la Torre, *Chem. Sci.* **2022**, *13*, 9249–9255.
- [34] V. S. P. K. Neti, M. R. Cerón, A. Duarte-Ruiz, M. M. Olmstead, A. L. Balch, L. Echegoyen, *Chem. Commun.* **2014**, *50*, 10584–10587.
- [35] C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671.

Manuscript received: August 3, 2023

Accepted manuscript online: September 11, 2023

Version of record online: September 21, 2023