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Dual molecular tweezers extending from a nanohoop†

M. Saeed Mirzaei,‡[a] Saber Mirzaei,‡[ac] Victor M. Espinoza Castro,[a]
Charlotte Lawrence[a] and Raúl Hernández Sánchez*[abc]

The field of nanohoops is mature enough that synthetic protocols exists to tune their size, composition (incorporation of heteroaromatic building blocks), connectivity (*para versus meta* linkages), and solubility in different media (hydrophobic *versus* hydrophilic). Here, we report an additional dimension incorporating the concept of fullerene tweezers into a nanohoop. The resulting hybrid nanohoop is highly strained at 77 kcal mol^{-1}, possesses a quantum yield of 0.12, emits at 584 nm, and displays a positive cooperative binding for C_{60} ($4K_2 \gg K_1$).

Realization of well-defined molecular compounds with radial π conjugation can be traced back to the late 90s in reports of anthracene dimers[1] and [*n*]cyclo-*para*-phenylacetylenes.[2] Later, the synthesis of nanohoops, or [*n*]cyclo-*para*-phenylenes ([*n*]CPPs), was described.[3,4] Their modular bottom up synthesis has led to a wide range of applications.[5] Since then, the field of conjugated aromatic macrocycles has expanded in many directions, including their use as novel building blocks for nanomaterials,[6] optoelectronic materials,[7] fluorophores,[8] polymers,[9] and in supramolecular recognition and sensing.[10] The curved nature of CPPs leads to weak intermolecular π–π stacking in solution; however, its cyclic nature creates an internal site suitable for hosting molecules that exhibit radial connectivity, *e.g.*, fullerenes, or another CPP.[11] Multiple literature reports describe CPPs binding fullerenes in a belt-like fashion.[12–21] Alternatively, an entire field exists centred around developing molecular tweezers – a molecular, bivalent, tweezer-like receptor containing two recognition subunits linked covalently – to bind fullerenes.[22] However, to the best of our knowledge, a nanohoop serving as a scaffold to create molecular tweezers has not been accomplished before.

Herein, we present **1** comprising a structure built with dibenzo[*a*,*c*]phenazine (DBP) repeating units which form the backbone of a strained conjugated aromatic macrocycle, or nanohoop, and also act as dual molecular tweezers for binding of C_{60}. The backbone of [8]CPP can be inscribed within the nanohoop portion of **1** (Fig. 1). It has been demonstrated that [8]CPP is too small to form a belt-like host:guest adduct with C_{60}, which only becomes possible with nanohoops containing at least ten *para*-phenylenes.[12,19,23] Thus, fullerene binding is proposed to take place in between the DBP units (*vide infra*), effectively creating dual molecular tweezers.

Dibenzo[*a*,*c*]phenazine, an electron acceptor with a half-wave reduction potential ($E_{1/2}$) of −1.35 V *vs.* Ag/Ag$^+$ in DMF,[24] was introduced into a nanohoop by using the known building block **S1** (ESI†).[25] A high-yielding and straightforward S_NAr reaction using 3,5-di-*tert*-butylphenol with K_2CO_3 in DMF led to **3a** (2.7 g, 93% yield). Miyaura borylation of **3a** catalyzed by Pd(dppf)Cl_2 led to **2** in 64% yield (Fig. 2a). Compound **1** was achieved by subjecting **2** to Pt(COD)Cl_2 and CsF in refluxing THF for 72 hours to form a square-shaped Pt metallacycle that was not isolated. Next, reductive elimination prompted by PPh_3

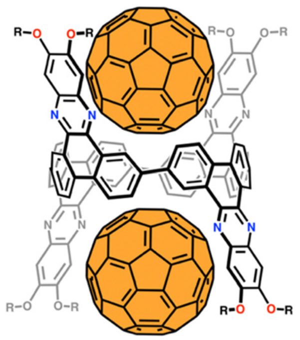

Fig. 1 Nanohoop-supported dual molecular tweezers **1** binding two equivalents of C_{60}. *R* = 3,5-di-*tert*-butylphenyl.

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[a] *Department of Chemistry, Rice University, 6100 Main St., Houston, Texas 77005, USA. E-mail: raulhs@rice.edu*
[b] *Rice Advanced Materials Institute, Rice University, Houston, Texas 77005, USA*
[c] *Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA*

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‡ These authors contributed equally to this work.

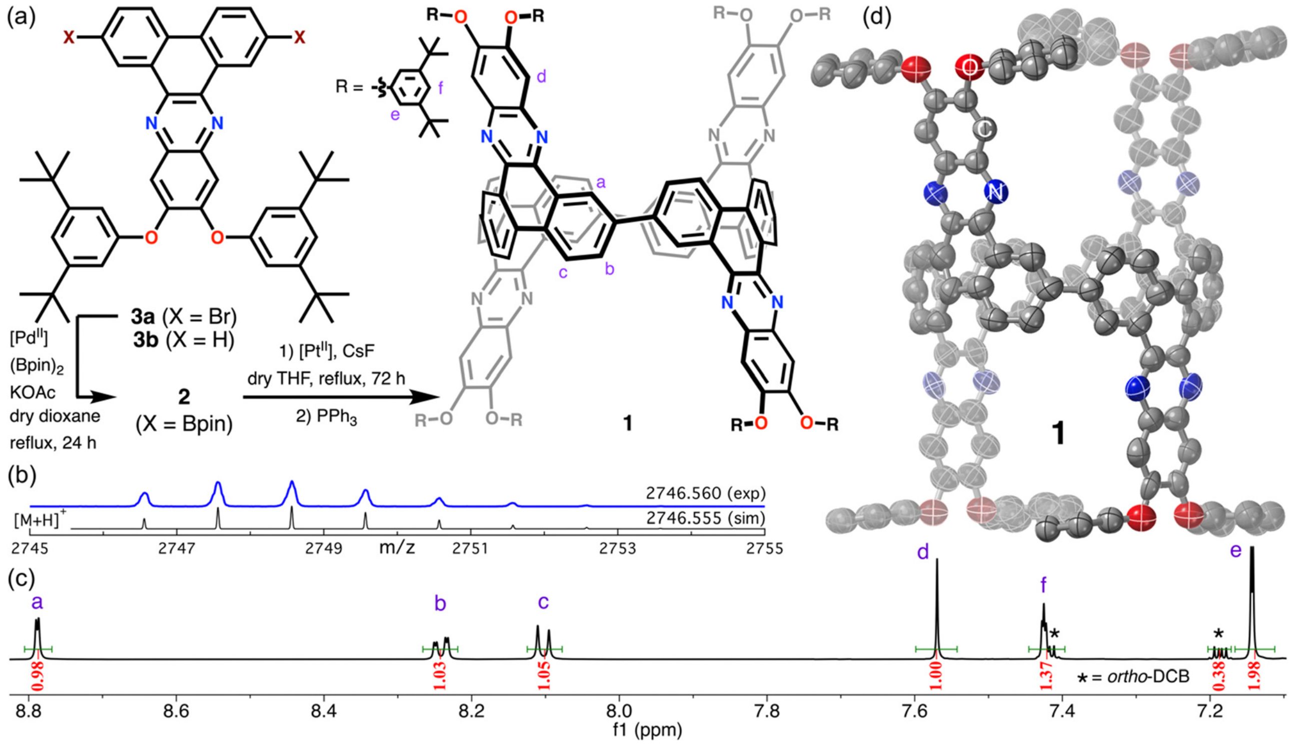

Fig. 2 Synthesis and characterization of **1**. (a) Two step synthetic protocol to get **1** from **3a**. (b) Experimental MALDI MS molecular ion peaks of **1** (blue trace). Black trace represents simulation of [M + H]$^+$ isotopic distribution. (c) Aromatic region of ^{1}H NMR of **1** collected in CD_2Cl_2 at 20 °C. (d) Molecular crystal structure of **1**. Thermal ellipsoids are set at 50% probability level. The H atoms and *tert*-butyl groups on the R group are removed for clarity.

led to **1** in 9% yield. MALDI-MS analysis of **1** (Fig. 2b) matches its expected molecular ion [M + H]$^+$. Moreover, ^{1}H NMR characterization displays a symmetric spectrum that to a first approximation could result from the D_{2d} or C_{4v} symmetric species (Fig. 2c). However, the assignment as D_{2d} was initially supported by DFT conformational analysis, where the D_{2d} isomer (1,3-alternate) is lowest in energy relative to the C_{4v} (cone), C_s (partial-cone), and C_{2h} (1,2-alternate) conformational isomers (Fig. S12, ESI†). All conformers fall within a relative energy window of 13 kcal mol^{-1}. Rotation of the DBP fragment in **1′** (R = Me) is highly disfavored, where DFT calculations indicate a rotational barrier of ∼30 kcal mol^{-1} (Fig. S13, ESI†). Thus, isomer interconversion is energetically prohibited at room temperature. Moreover, DFT calculations at the B3LYP/6-31G(d) level of theory concluded that contortion in **1′** results in 77 kcal mol^{-1} of strain energy (Fig. S14, ESI†). Interestingly, this value is only slightly higher than that reported for [8]CPP at 72.2 kcal mol^{-1},[26] even though **1** only has four single bonds along the nanohoop fragment with DBP units likely bending away from planarity. Finally, definitive structural assignment was obtained from single-crystal X-ray diffraction. Crystals of **1** were grown from vapor diffusion of MeCN into a solution of **1** in *ortho*-dichlorobenzene/DCM (1 : 1). The molecular crystal structure of **1** (Fig. 2d) displays a cylindrical shape whose diameter measured at the nanohoop fragment is 11.12(7) Å.

Species **1** is a bright yellow powder with its lowest energy absorption peak located at λ_{max} of 412 nm (Fig. 3). It also displays several absorption bands at higher energies with discernable peaks at 393, 354, and 283 nm. Time-dependent DFT (TD-DFT) analysis supported the assignment of these absorption bands. Our calculations show that the absorption at 412 nm corresponds to the HOMO−1 or HOMO−2 → LUMO transition (Table S2, ESI†). In fact, comparing with compound **3b** indicates that most of the observed transitions result from the dibenzo[*a*,*c*]phenazine fragment (Fig. 3). However, the transition at 354 nm is unique to **1** and based on our calculations it seems to arise from HOMO−6 → LUMO. Additionally, the HOMO → LUMO transition in **1′** is symmetry forbidden

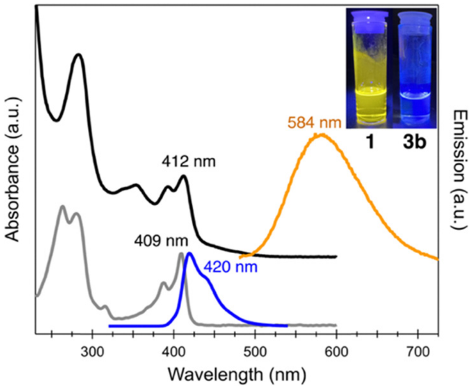

Fig. 3 Absorption and emission profile of **1** (black and orange traces) and **3b** (grey and blue traces) in CH_2Cl_2 at room temperature. Emission data were collected by light excitation at 350 nm. Inset: Photographic image of a solution of **1** and **3b** in CH_2Cl_2 irradiated with UV light.

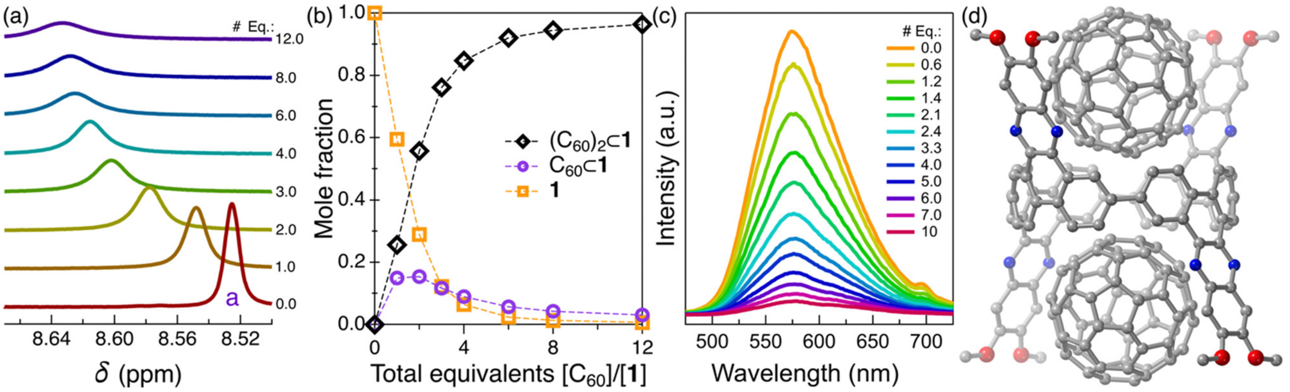

Fig. 4 (a) ^{1}H NMR titration of C_{60} into 1 in 1,1,2,2-tetrachloroethane-d$_2$ at 20 °C. Shift of resonance "a" is shown as labelled in Fig. 2a. (b) Mole fraction of 1, $C_{60}\subset 1$, and $(C_{60})_2\subset 1$ obtained from fitting NMR data in (a) to a 1 : 2 host : guest model using Bindfit. (c) Fluorescence quenching titration of 1 with C_{60} in 1,1,2,2-tetrachloroethane. (d) DFT optimized structure of $(C_{60})_2\subset 1$ at the B3LYP-D3BJ/6-31G* + PCM(CH_2Cl_2) level of theory.

(f = 0.0), consistent with [n]CPPs.[27] Our DFT results show both the HOMO and LUMO delocalized symmetrically across **1′**, the former is localized exclusively across the nanohoop fragment, while the latter presents orbital density on the entire molecule (Fig. S15, ESI†).

Nanohoops with emission past 550 nm are rare.[28–31] We noticed a bright orange solution when **1** is dissolved in dichloromethane and exposed to UV light. Unlike other bright nanohoop fluorophores,[29] compound **1** displays a mild fluorescence solvatochromism (Fig. S16, ESI†). The visual comparison between emission from **1** and **3b** is markedly different (Fig. 3 inset). In **1**, the emission envelope is characterized by a broad band with peak at λ_{em} of 584 nm. In stark contrast, **3b** emits with λ_{em} at 420 nm. Intrigued by the emissive properties of **1**, we determined its quantum yield (ϕ, ESI†). Compound **1** has a ϕ of 0.12, which is slightly higher than that of [8]CPP (0.084),[32] but lower than nanohoops with the highest quantum yields reported to date, *e.g.*, [10–12]CPP (ϕ = 0.46 to 0.81),[33,34] BT[10]CPP (ϕ = 0.59),[35] and TB[12]CPP (ϕ = 0.59 to 0.98).[36] Last, the red-shifted emission in **1** relative to **3b** likely results from extended π delocalization across all four DBP units.

Since the architecture of **1** combines design principles related to conjugated aromatic macrocycles and molecular tweezers, we hypothesized that **1** could serve as an ideal host for C_{60}. To demonstrate the fullerene hosting properties of **1**, we performed ^{1}H NMR titration experiments by adding C_{60} to a solution of **1** in 1,1,2,2-tetrachloroethane – a solvent that enhances the solubility of C_{60}.[37] The data shown in Fig. 4a displays a downfield shift of resonance "a" with increasing equivalents of C_{60}. Note that resonances "b" and "c" show a mild upfield shift when C_{60} is added into **1** (Fig. S18, ESI†). The data in Fig. 4a does not fit to a 1 : 1 host : guest (H : G) model when analyzed using Bindfit, but instead fits well to a 1 : 2 system with $K_1 = 149\ M^{-1}$ and $K_2 = 1021\ M^{-1}$ (Fig. S19, ESI†).[38] The resulting mole fraction obtained from the fit is shown in Fig. 4b, and clearly indicates a positive cooperative effect[39,40] where the intermediate 1 : 1 H : G is almost absent.[41] Moreover, fluorescence quenching experiments were conducted to further examine C_{60} binding into **1**. Analysis of the data in Fig. 4c using a 1 : 2 H : G model provides values of $K_1 = 1956\ M^{-1}$ and $K_2 = 4311\ M^{-1}$ (Fig. S20, ESI†). While the magnitude of K_1 and K_2 between the two methods do not match, the overall trend in the association constants reflect the same positive cooperativity, that is $4K_2 \gg K_1$, and confirms our initial hypothesis that **1** functions as dual molecular tweezers hosting two molecules of C_{60}. It is important to highlight that a single molecular host accommodating two fullerene species is rare.[42–45] Finally, to visualize the 1 : 2 host : guest adduct, a DFT model was optimized and is shown in Fig. 4d. As observed from the structure, the DBP units are pushed out to accommodate the C_{60} guests. The distortion of **1** upon C_{60} binding may explain the positive cooperative effect. Last, non-covalent interactions mainly take place between the DBP units and C_{60} with little contribution from the nanohoop as visualized in the contact surface obtained from the independent gradient model based on Hirshfeld partition of molecular density (IGMH, Fig. S22, ESI†).[46]

In summary, we report an orange emitting dual molecular tweezers–nanohoop which is capable of simultaneously hosting two C_{60} molecules with moderate affinity. We anticipate that the present work will pave the way towards extended nanohoop-tweezers to develop applications in optoelectronic devices and supramolecular materials.

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Data availability

Data supporting this article have been included in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 S. Kammermeier, P. G. Jones and R. Herges, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2669–2671.
2 T. Kawase, H. R. Darabi and M. Oda, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2664–2666.
3 R. Jasti, J. Bhattacharjee, J. B. Neaton and C. R. Bertozzi, *J. Am. Chem. Soc.*, 2008, **130**, 17646–17647.
4 D. Wu, W. Cheng, X. Ban and J. Xia, *Asian J. Org. Chem.*, 2018, **7**, 2161–2181.
5 S. Mirzaei, E. Castro and R. Hernández Sánchez, *Chem. – Eur. J.*, 2021, **27**, 8642–8655.
6 H. Omachi, T. Nakayama, E. Takahashi, Y. Segawa and K. Itami, *Nat. Chem.*, 2013, **5**, 572–576.
7 Y. Xu, M.-Y. Leung, L. Yan, Z. Chen, P. Li, Y.-H. Cheng, M. H.-Y. Chan and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2024, **146**, 13226–13235.
8 B. M. White, Y. Zhao, T. E. Kawashima, B. P. Branchaud, M. D. Pluth and R. Jasti, *ACS Cent. Sci.*, 2018, **4**, 1173–1178.
9 G. M. Peters, G. Grover, R. L. Maust, C. E. Colwell, H. Bates, W. A. Edgell, R. Jasti, M. Kertesz and J. D. Tovar, *J. Am. Chem. Soc.*, 2020, **142**, 2293–2300.
10 D. Lu, Q. Huang, S. Wang, J. Wang, P. Huang and P. Du, *Front. Chem.*, 2019, **7**, 668.
11 M. B. Minameyer, Y. Xu, S. Frühwald, A. Görling, M. von Delius and T. Drewello, *Chem. – Eur. J.*, 2020, **26**, 8729–8741.
12 T. Iwamoto, Y. Watanabe, T. Sadahiro, T. Haino and S. Yamago, *Angew. Chem., Int. Ed.*, 2011, **50**, 8342–8344.
13 T. Iwamoto, Y. Watanabe, H. Takaya, T. Haino, N. Yasuda and S. Yamago, *Chem. – Eur. J.*, 2013, **19**, 14061–14068.
14 H. Isobe, S. Hitosugi, T. Yamasakia and R. Iizukaa, *Chem. Sci.*, 2013, **4**, 1293–1297.
15 Y. Nakanishi, H. Omachi, S. Matsuura, Y. Miyata, R. Kitaura, Y. Segawa, K. Itami and H. Shinohara, *Angew. Chem., Int. Ed.*, 2014, **53**, 3102–3106.
16 I. González-Veloso, E. M. Cabaleiro-Lago and J. Rodríguez-Otero, *Phys. Chem. Chem. Phys.*, 2018, **20**, 11347–11358.
17 Y. Xu, B. Wang, R. Kaur, M. B. Minameyer, M. Bothe, T. Drewello, D. M. Guldi and M. V. Delius, *Angew. Chem., Int. Ed.*, 2018, **57**, 11549–11553.
18 T. C. Lovell, S. G. Bolton, J. P. Kenison, J. Shangguan, C. E. Otteson, F. Civitci, X. Nan, M. D. Pluth and R. Jasti, *ACS Nano*, 2021, **15**, 15285–15293.
19 F. Bernt and H. A. Wegner, *Chem. – Eur. J.*, 2023, **29**, e202301001.
20 Y. Xu, F. Steudel, M.-Y. Leung, B. Xia, M. V. Delius and V. W.-W. Yam, *Angew. Chem., Int. Ed.*, 2023, **62**, e202302978.
21 X. Chang, Y. Xu and M. V. Delius, *Chem. Soc. Rev.*, 2024, **53**, 47–83.
22 E. M. Pérez and N. Martín, *Pure Appl. Chem.*, 2010, **82**, 523–533.
23 Y. Nagasawa and S. Okada, *J. Phys. Soc. Jpn.*, 2017, **86**, 104702.
24 B. J. Tabner and J. R. Yandle, *J. Chem. Soc. A*, 1968, 381–388, DOI: 10.1039/J19680000381.
25 K. Wang, P. Jiang, Z.-G. Zhang, Q. Fu and Y. Li, *Macromol. Chem. Phys.*, 2013, **214**, 1772–1779.
26 Y. Segawa, H. Omachi and K. Itami, *Org. Lett.*, 2010, **12**, 2262–2265.
27 T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki and S. Yamago, *J. Am. Chem. Soc.*, 2011, **133**, 8354–8361.
28 E. R. Darzi, E. S. Hirst, C. D. Weber, L. N. Zakharov, M. C. Lonergan and R. Jasti, *ACS Cent. Sci.*, 2015, **1**, 335–342.
29 T. Kuwabara, J. Orii, Y. Segawa and K. Itami, *Angew. Chem., Int. Ed.*, 2015, **54**, 9646–9649.
30 D. Ari, E. Dureau, O. Jeannin, J. Rault-Berthelot, C. Poriel and C. Quinton, *Chem. Commun.*, 2023, **59**, 14835–14838.
31 V. Bliksted Roug Pedersen, T. W. Price, N. Kofod, L. N. Zakharov, B. W. Laursen, R. Jasti and M. Brøndsted Nielsen, *Chem. – Eur. J.*, 2024, **30**, e202303490.
32 M. Fujitsuka, D. W. Cho, T. Iwamoto, S. Yamago and T. Majima, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14585–14588.
33 E. R. Darzi, T. J. Sisto and R. Jasti, *J. Org. Chem.*, 2012, **77**, 6624–6628.
34 M. Fujitsuka, C. Lu, B. Zhuang, E. Kayahara, S. Yamago and T. Majima, *J. Phys. Chem. A*, 2019, **123**, 4737–4742.
35 T. C. Lovell, Z. R. Garrison and R. Jasti, *Angew. Chem., Int. Ed.*, 2020, **59**, 14363–14367.
36 Z.-L. Qiu, C. Tang, X.-R. Wang, Y.-Y. Ju, K.-S. Chu, Z.-Y. Deng, H. Hou, Y.-M. Liu and Y.-Z. Tan, *Angew. Chem., Int. Ed.*, 2020, **59**, 20868–20872.
37 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379–3383.
38 https://supramolecular.org/.
39 A. D. Hughes and E. V. Anslyn, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6538–6543.
40 D. H. Williams and M. S. Westwell, *Chem. Soc. Rev.*, 1998, **27**, 57–64.
41 P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305–1323.
42 K. Miki, T. Matsushita, Y. Inoue, Y. Senda, T. Kowada and K. Ohe, *Chem. Commun.*, 2013, **49**, 9092–9094.
43 K. Li, Z. Xu, H. Deng, Z. Zhou, Y. Dang and Z. Sun, *Angew. Chem., Int. Ed.*, 2021, **60**, 7649–7653.
44 X. Zhang, H. Shi, G. Zhuang, S. Wang, J. Wang, S. Yang, X. Shao and P. Du, *Angew. Chem., Int. Ed.*, 2021, **60**, 17368–17372.
45 L. Zhan, C. Dai, G. Zhang, J. Zhu, S. Zhang, H. Wang, Y. Zeng, C. H. Tung, L. Z. Wu and H. Cong, *Angew. Chem., Int. Ed.*, 2022, **61**, e202113334.
46 T. Lu and Q. Chen, *J. Comput. Chem.*, 2022, **43**, 539–555.