

2,3:6,7-Naphthalene Bis(dicarboximide) Cyclophane: A Photofunctional Host for Ambient Delayed Fluorescence in Solution

Swadhin Garain⁺, Pei-Lun Li⁺, Kazutaka Shoyama, and Frank Würthner*

Abstract: Harvesting triplet excitons of heavy atom-free purely organic chromophores under aerated conditions is challenging due to the quenching of long-lived triplet states by molecular oxygen and vibrational dissipation. Herein, we show a supramolecular approach of triplet harvesting via mitigating quenching pathways of a triplet harvester. Specifically, we used a host-guest system based on 2,3:6,7-naphthalene bis(dicarboximide)-derived cyclophane (**NBICy**) and carbazole derivative (**EtCz**). Complexation studies and single-crystal X-ray analysis showed the formation of a rigid host-guest complex ($K \approx 10^4 \text{ M}^{-1}$ in CCl_4), resulting in triplet-exciton stabilization under aerated conditions via mitigating vibrational interference and oxygen quenching. Photophysical studies elucidate the delayed fluorescence emission from the charge-transfer state (^1CT) with a quantum yield (QY) of 6–8 % under ambient conditions which increased up to 36 % in an inert atmosphere.

Thermally activated delayed fluorescence (TADF) is a key element of triplet harvesting technology, revolutionizing the materials design for light emitting organic devices such as organic light emitting diodes (OLEDs) or organic photodetectors (OPDs).^[1] TADF emitters are typically organic π -conjugated molecules, consisting of a covalently linked donor-acceptor motif to minimize the singlet-triplet energy gap.^[1a-c] However, under such design principles, TADF emitters suffer from exciton quenching by molecular oxygen species, becoming inactive in solution state under ambient conditions, whilst successful in solid state material.^[1] Moreover, purely organic phosphors demand suitable triplet-state stabilization techniques, heavy atom-induced intersystem crossing, and spin-orbit coupling for solution-phase phos-

phorescence emission.^[2] Thus, it is challenging to design triplet harvesters that can be utilized in solution state under aerated conditions, e.g. for sensing, bio-imaging, and photocatalysis.^[3] In order to mitigate oxygen quenching and vibrational dissipation in solution state under aerated conditions, few groups developed heavy atom substituted organic phosphors and used cucurbit[n]uril hosts^[4] or supramolecular scaffolding approaches to achieve phosphorescence emission.^[5,6] We contemplated an alternative method to produce ambient-stable (i.e. tolerant to molecular oxygen-induced quenching of triplet exciton) triplet harvesters design of host-guest systems composed of heavy atom-free purely organic chromophores in a solution state. Toward this goal, cyclophanes appeared most promising because they embed π -conjugated guest molecules from two faces, thereby providing sufficient binding strength to ensure complex formation in dilute solution.^[7]

Here we show an ambient active TADF emitting host-guest system employing 2,3:6,7-naphthalene bis(dicarboximide)-derived cyclophane (**NBICy**) host and *n*-ethylcarbazole (**EtCz**) guest. Host-guest complexation experiments showed that **NBICy** host and **EtCz** guest form a robust host-guest complex with a binding constant up to 10^4 M^{-1} (Figure 1). Most interestingly, in aerated solution the **EtCz**=**NBICy** complex shows delayed fluorescence at a sub-microsecond time scale in nonpolar and polar solvents. To the best of our knowledge, this is the first observation for ambient delayed fluorescence via a non-covalent approach using host-guest strategy in solution state. We attribute the ambient triplet exciton stability of **EtCz**=**NBICy** to its robust host-guest structure, which helps to restrict oxygen quenching and vibrational interference, crucial for ambient triplet stability. Further, the efficient triplet generation ability of **NBICy** ($k_{\text{ISC}} \approx 10^7 \text{ s}^{-1}$) and fast reverse intersystem crossing ($k_{\text{RISC}} \approx 10^6\text{--}10^5 \text{ s}^{-1}$) to the emissive charge-transfer (CT) state (**EtCz**=**NBICy**)* helps for delayed fluorescence

[*] Dr. S. Garain,⁺ P.-L. Li,⁺ Dr. K. Shoyama, Prof. Dr. F. Würthner
Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
E-mail: wuerthner@uni-wuerzburg.de

Dr. K. Shoyama, Prof. Dr. F. Würthner
Center for Nanosystems Chemistry (CNC), Universität Würzburg, Theodor-Boveri-Weg, 97074 Würzburg, Germany

[⁺] Contributed equally to this work.

© 2024 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 License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

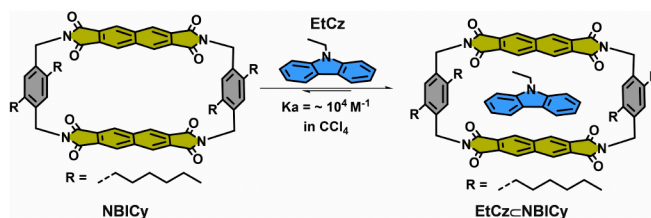


Figure 1. Chemical structure of 2,3:6,7-naphthalene bis(dicarboximide) cyclophane (**NBICy**), *n*-ethylcarbazole (**EtCz**) guest and host-guest complex (**EtCz**=**NBICy**).

emission being observable in the aerated solution state ($\Phi = 6-8\%$). The efficient generation of CT state is further validated by single-crystal X-ray diffraction analysis, which showed shape-complementarity of the host-guest complex and close $\pi-\pi$, C-H- π , and CT interactions.

NBICy cyclophane was synthesized via one-pot imidization reaction of (2,5-dihexyl-1,4-phenylene)dimethanamine and 2,3:6,7-naphthalene dianhydride in an acetic acid/toluene mixture. The product was characterized by ^1H , ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis (see Supporting Information for detailed synthetic procedure, Schemes S1,S2).

Next, we determined the binding constant of the host-guest complex (**EtCz=NBICy**) using ^1H NMR titration

Table 1: Binding constants K (M^{-1}) and Gibbs free energies ΔG^0 (kJ mol^{-1}) of 1:1 host-guest complexes.

Solvent ^[a]	$K \text{ (M}^{-1}\text{)}^{[b]}$	$\Delta G^{0[c]} \text{ (kJ mol}^{-1}\text{)}$
Carbon tetrachloride: Chloroform (3:1)	$(2.0 \pm 0.2) \times 10^4$	-24.3
Chloroform	$(9.6 \pm 1.5) \times 10^2$	-16.8
Tetrahydrofuran	$(1.2 \pm 0.05) \times 10^3$	-17.5
Tetrachloroethane	$(7.3 \pm 0.05) \times 10^2$	-16.2

[a] All ^1H NMR titrations were performed using the deuterated solvents. [b] Association constants (K) were determined by fitting ^1H NMR titration data using the 1:1 binding model of program `bindfit`^[8] at 295 K. [c] Gibbs free energies ΔG^0 (295 K) calculated from K according to ΔG^0 (295 K) = $-RT\ln K$. All the experimental data and mole fraction plots are given in the Supporting Information. All binding constants reported are within 0.5 kJ mol^{-1} of error in Gibbs free energy.

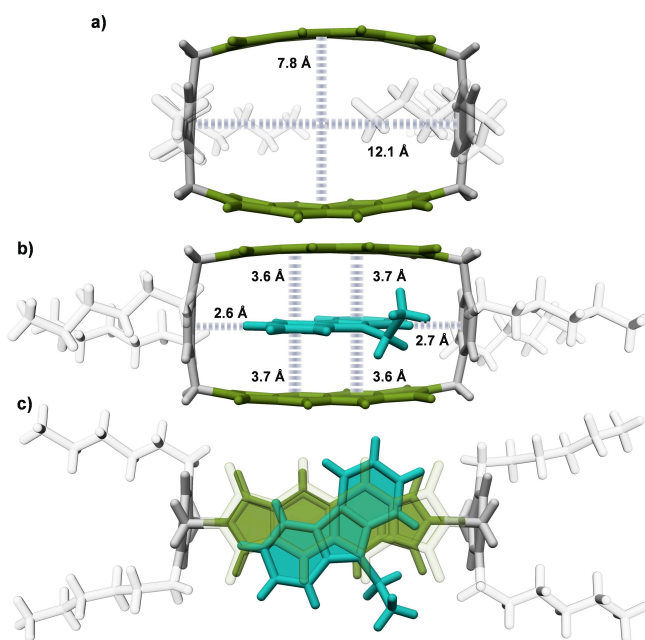


Figure 2. Single-crystal X-ray analysis: (a) The front view of the **NBICy** host. (b) Side view and (c) top view of the **EtCz**–**NBICy** complex showing stabilization of the guest inside the cyclophane by π – π and C–H– π interactions.

studies in different solvents with varying polarity as summarized in Table 1 (see also Figures S1–S4). The non-polar CCl_4 endows high association strength compared to the other more polar solvent. Further, it can solubilize the host better than any other non-polar solvents via dispersion interaction.

Single crystals of the individual host and the host-guest complexes suitable for crystallographic analysis were obtained upon slow vapor diffusion of methanol into the chloroform solution (Figures 2a–c, S5,S6, Table S1,S2). Single-crystal X-ray analysis revealed that **NBICy** formed a nano-cavity with a distance between two naphthalene bisimide and linker units of 7.8 Å and 12.1 Å, respectively, suggesting **NBICy** is ideal for carbazole guest binding (Figures 2a, S5). Interestingly, single crystal X-ray analysis of the host-guest complex revealed that **EtCz** is stabilized in the **NBICy** cavity through both π - π (3.6 /3.7 Å) and C-H- π (2.6 /2.7 Å) interactions (Figures 2b,c, S6). It is essential to mention here that π - π interaction between the electron-rich carbazole unit and the electron-deficient naphthalene bisimide unit is also a prerequisite for the formation of CT state formation.^[9] Theoretical calculations of the **EtCz**=**NBICy** host-guest complex showed that the highest occupied molecular orbital (HOMO) is located on the electron-rich carbazole derivative and the lowest occupied molecular

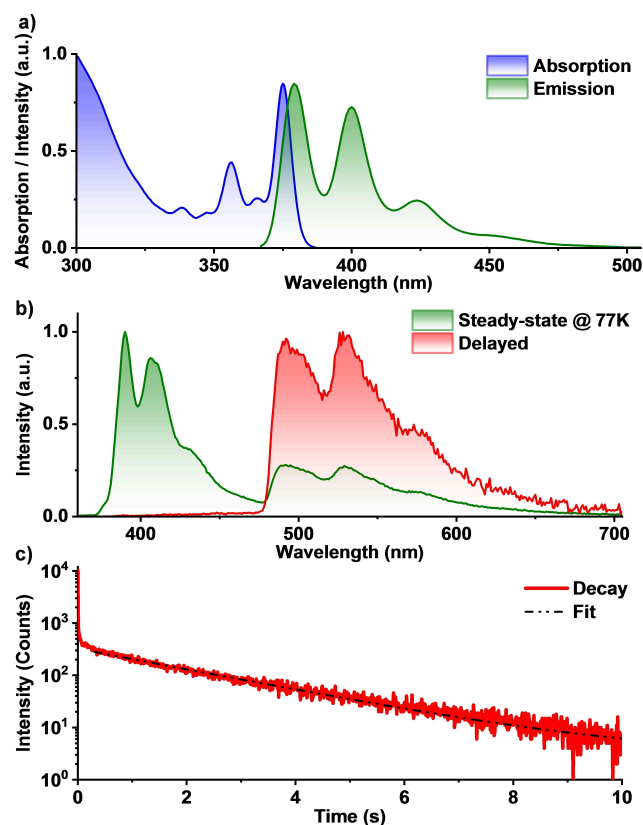


Figure 3. (a) Normalized UV/Visible absorption and corresponding steady-state emission spectra of **NBICy** in CCl_4 at 295 K. (b) Steady-state (green line), delayed (red line) emission spectra and c) phosphorescence lifetime decay profile of **NBICy** in CHCl_3 at 77 K ($\lambda_{\text{ex}} = 345 \text{ nm}$, delay time = 2 ms, $c(\text{NBICy}) = 2.52 \times 10^{-5} \text{ M}$).

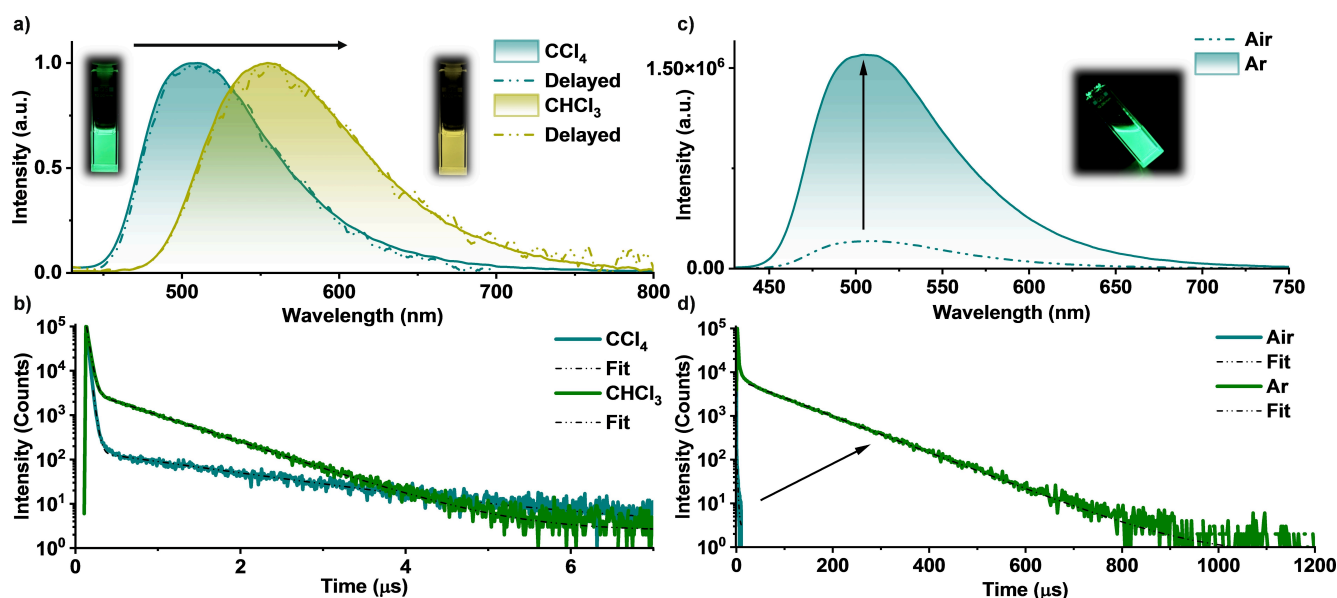


Figure 4. Delayed fluorescence studies of **EtCz=NBICy** host-guest complex in solution at 295 K: (a) Steady-state and delayed emission spectra in CCl₄ and CHCl₃ showing bathochromic shift and delayed fluorescence in air. (b) The lifetime decay profile in CCl₄ and CHCl₃ shows prompt and delayed fluorescence in air. (c) Steady-state emission spectra and (d) lifetime decay profile under air and argon atmosphere, showing a significant increase of the delayed emission and lifetime upon argon purging, confirming the triplet contribution of the CT emission. (For all cases, $\lambda_{\text{ex}}=405$ nm, $\lambda_{\text{obs}}=510$ nm, and 560 nm for CCl₄ and CHCl₃ respectively, delay time = 50 μ s, $c[\text{NBICy}]=2.5\times 10^{-5}$ M, $c[\text{EtCz}]=1.1\times 10^{-3}$ M and 2.0×10^{-3} M for CCl₄ and CHCl₃ respectively).

orbital (LUMO) is located on the electron deficient naphthalene bisimide unit, confirming the possibility of CT transitions upon host-guest complexation (Figure S7).

Next, we recorded the UV-Vis absorption spectra of **NBICy** host in CCl₄, which showed broad S_0-S_2 transition in the high energy region (<300 nm) and S_0-S_1 transitions spanning from ~340 to 370 nm with pronounced vibrational progression which maximizes at 375 nm and 355 nm (Figures 3a, S8). Corresponding emission spectra also showed vibrational characteristics with a maximum of 378 nm and spanned up to 500 nm ($\lambda_{\text{ex}}=345$ nm) (Figure 3a). Next, to find out the hidden phosphorescence emission band of the **NBICy**, we performed the photoluminescence study at 77 K, and we observed a vibronically featured locally excited phosphorescence emission (^3LE), which maximizes at 490 and 530 nm ($\lambda_{\text{ex}}=345$ nm) (Figure 3b). The long-lived nature of the emission is further confirmed by delayed emission spectra (delay time = 2 ms) and lifetime decay profile shown in Figures 3b,c ($\tau_p=2.12$ s).

Next, we performed a photophysical studies of the **EtCz=NBICy** host-guest complex in the solution state in non-polar and polar solvents. The **EtCz=NBICy** host-guest complex formed a broader and more red-shifted absorption band (ranging from 375 nm to 500 nm) compared to the individual host and guest in CCl₄, CHCl₃, TCE, and THF (Figure S8). Interestingly, corresponding emission spectra revealed a bathochromic shift from nonpolar to polar solvent, demonstrating the CT nature of the emission ($\lambda_{\text{ex}}=405$ nm), which is further confirmed by the excitation spectra ($\lambda_{\text{obs}}=510$ nm and 560 nm for CCl₄ and other solvents respectively) (Figures 4a,S9). The photophysical study vali-

dated our hypothesis of emissive CT state formation upon complexation. Most interestingly, the lifetime decay profile of the emissive CT state showed a bi-exponential lifetime decay profile with a fast prompt fluorescence and delayed fluorescence with triplet contribution in all the studied solvents under air. The lifetime of the prompt fluorescence is ~30 to ~50 ns, and delayed fluorescence is ~0.5 to ~1.5 μ s under aerated conditions (Figures 4b,S10–13, Table S3). The delayed fluorescence nature was further corroborated by the delayed emission spectra (delay time = 50 μ s) (Figures 4a,S10–13, Table S3). We attested the triplet contribution to the CT emission in an oxygen-free atmosphere, which resulted in a significant increase in the emission intensity and lifetime, unambiguously proving the delayed fluorescence nature of the CT emission with significant triplet contribution (Figures 4c,d,S10–13, Table S4). A temperature-dependent study further helped us to conclude that delayed fluorescence emission is a thermally activated process, which also explained the role of **NBICy** triplet state (^3LE) for achieving ambient delayed fluorescence in solution. (Figure S14, Table S5). This experimental observation showcases the potential of heavy atom-free supramolecular host-guest complexes for triplet harvesting in the air. The observed delayed fluorescence quantum yield of **EtCz=NBICy** is 6–8 % indeed quite remarkable in air, and increases to 36 %, 21 %, and 10 % in CCl₄, CHCl₃, and THF, respectively, under argon atmosphere. The excellent triplet formation ability of the **NBICy** cyclophane with very high ISC and RISC rate ($k_{\text{ISC}}\approx 10^7$ s⁻¹, $k_{\text{RISC}}\approx 10^6$ – 10^5 s⁻¹) is liable for ambient triplet stability and achieving high quantum yield up to 36 % in solution state. Notably,

the **EtCz=NBICy** complex also showed efficient delayed fluorescence in the solid state under aerated conditions, pointing the potential of this complex for future OLED technology (Figure S15, Table S6).^[1e]

In conclusion, we have demonstrated ambient triplet harnessing in a novel 2,3:6,7-naphthalene bis(dicarboximide)-derived cyclophane (**NBICy**) and *n*-ethyl carbazole (**EtCz**) guest in the solution state capitalizing the binding strength provided by cyclophanes by two interacting π -surfaces. Our spectroscopic observations revealed that **EtCz=NBICy** host–guest complex showed ambient delayed fluorescence emission in non-polar and polar solvents. The triplet contribution of the delayed fluorescence emission was unambiguously proved under an inert atmosphere and by temperature-dependent studies. Single-crystal X-ray analysis further elucidated the role of rigid supramolecular structure in restricting vibrational dissipation, oxygen diffusion, and CT state formation for delayed fluorescence emission. We believe that the non-covalent supramolecular approach of triplet harnessing will open diverse opportunities for the utilization of organic triplets in bio-imaging, sensing, and photocatalysis.

Acknowledgements

We thank the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program for financial support (grant agreement no. 787937; recipient F.W.). We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III and we would like to thank Dr. Johanna Hakanpää for assistance in using P11. Beamtime was allocated for proposal I-20231007. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All the Additional spectroscopic, NMR titration and all additional data underlying this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.11652411>.

Accession Codes: CCDC2361985, CCDC2361986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Keywords: Host–guest Systems • Cyclophane • Photochemistry • Supramolecular Chemistry • Delayed Fluorescence

- [1] a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, *492*, 234–238; b) P. L. dos Santos, M. K. Etherington, A. P. Monkman, *J. Mater. Chem. C* **2018**, *6*, 4842–4853; c) M. Y. Wong, E. Zysman-Colman, *Adv. Mater.* **2017**, *29*, 1605444; d) S. Hirata, *Adv. Opt. Mater.* **2017**, *5*, 170011; e) C.-Y. Lin, C.-H. Hsu, C.-M. Hung, C.-C. Wu, Y.-H. Liu, E. H.-C. Shi, T.-H. Lin, Y. C. Hu, W.-Y. Hung, K.-T. Wong, P.-T. Chou, *Nat. Chem.* **2024**, *16*, 98–106; f) H.-Y. Zhou, D.-W. Zhang, M. Li, C.-F. Chen, *Angew. Chem. Int. Ed.* **2022**, *61*, e202117872; *Angew. Chem.* **2022**, *134*, e202117872; g) N. Xue, H. Y. Zhou, Y. Han, M. Li, H. Y. Lu, C.-F. Chen, *Nat. Commun.* **2024**, *15*, 1425; h) H. Tsujimoto, D.-G. Ha, G. Markopoulos, H. S. Chae, M. A. Baldo, T. M. Swager, *J. Am. Chem. Soc.* **2017**, *139*, 4894–4900.
- [2] a) D. Sasikumar, A. T. John, J. Sunny, M. Hariharan, *Chem. Soc. Rev.* **2020**, *49*, 6122–6140; b) M. A. Niyas, R. Ramakrishnan, V. Vijay, E. Sebastian, M. Hariharan, *J. Am. Chem. Soc.* **2019**, *141*, 4536–4540; c) K. Vinod, S. D. Jadhav, M. Hariharan, *Chem. A Eur. J.* **2024**, e202400499; d) A. D. Nidhankar, Goudappagouda, V. C. Wakchaure, S. S. Babu, *Chem. Sci.* **2021**, *12*, 4216–4236; e) A. D. Nidhankar, Goudappagouda, D. S. Mohana Kumari, S. K. Chaubey, R. Nayak, R. G. Gonnade, G. V. P. Kumar, R. Krishnan, S. S. Babu, *Angew. Chem. Int. Ed.* **2020**, *59*, 13079–13085; *Angew. Chem.* **2020**, *132*, 13179–13185; f) M. J. Sun, O. Anhalt, M. B. Sárosi, M. Stolte, F. Würthner, *Adv. Mater.* **2022**, *34*, No. 2207331.
- [3] a) A. Fermi, G. Bergamini, M. Roy, M. Gingras, P. Ceroni, *J. Am. Chem. Soc.* **2014**, *136*, 6395–6400; b) M. Villa, B. Del Secco, L. Ravotto, M. Roy, E. Rampazzo, N. Zaccheroni, L. Prodi, M. Gingras, S. A. Vinogradov, P. Ceroni, *J. Phys. Chem. C* **2019**, *123*, 29884–29890; c) K. Y. Zhang, Q. Yu, H. Wei, S. Liu, Q. Zhao, W. Huang, *Chem. Rev.* **2018**, *118*, 1770–1839; d) A. Garci, J. A. Weber, R. M. Young, M. Kazem-Rostami, M. Ovalle, Y. Beldjoudi, A. Atilgan, Y. J. Bae, W. Liu, L. O. Jones, C. L. Stern, G. C. Schatz, O. K. Farha, M. R. Wasielewski, J. F. Stoddart, *Nat. Catal.* **2022**, *5*, 524–533; e) M. Bryden, E. Zysman-Colman, *Chem. Soc. Rev.* **2021**, *50*, 7587–7680.
- [4] a) F. Biedermann, E. Elmalem, I. Ghosh, W. M. Nau, O. A. Scherman, *Angew. Chem. Int. Ed.* **2012**, *51*, 7739–7743; *Angew. Chem.* **2012**, *124*, 7859–7863; b) A. C. Bhasikuttan, J. Mohanty, W. M. Nau, H. Pal, *Angew. Chem. Int. Ed.* **2007**, *46*, 4120–4122; *Angew. Chem.* **2007**, *119*, 4198–4200.
- [5] a) X. Ma, Y. Liu, *Acc. Chem. Res.* **2021**, *54*, 3403–3414; b) D. Li, F. Lu, J. Wang, W. Hu, X. Cao, X. Ma, H. Tian, *J. Am. Chem. Soc.* **2018**, *140*, 1916–1923; c) Y. Gong, H. Chen, X. Ma, H. Tian, *ChemPhysChem* **2016**, *17*, 1934–1938; d) J. Wang, Z. Huang, X. Ma, H. Tian, *Angew. Chem. Int. Ed.* **2020**, *59*, 9928–9933; *Angew. Chem.* **2020**, *132*, 10014–10019; e) H. Yu, Q. Zhou, X. Dai, F. Shen, Y. Zhang, X. Xu, Y. Liu, *J. Am. Chem. Soc.* **2021**, *143*, 13887–13894; f) X.-K. Ma, W. Zhang, Z. Liu, H. Zhang, B. Zhang, Y. Liu, *Adv. Mater.* **2021**, *33*, 2007476; g) S. Garain, B. C. Garain, M. Eswaramoorthy, S. K. Pati, S. J. George, *Angew. Chem. Int. Ed.* **2021**, *60*, 19720–19724; *Angew. Chem.* **2021**, *133*, 19872–19876.
- [6] a) S. Garain, S. M. Wagalgave, A. A. Kongasseri, B. C. Garain, S. N. Ansari, G. Sardar, D. Kabra, S. K. Pati, S. J. George, *J. Am. Chem. Soc.* **2022**, *144*, 10854–10861; b) S. Kuila, K. V. Rao, S. Garain, P. K. Samanta, S. Das, S. K. Pati, M. Eswaramoorthy, S. J. George, *Angew. Chem. Int. Ed.* **2018**, *57*, 17115–17119; *Angew. Chem.* **2018**, *130*, 17361–17365.
- [7] a) P. Spent, F. Würthner, *Angew. Chem. Int. Ed.* **2015**, *54*, 10165–10168; *Angew. Chem.* **2015**, *127*, 10303–10306; b) J. C. Barnes, M. Juricek, N. L. Strutt, M. Frascioni, S. Sampath, M. A.

- Giesener, P. L. McGrier, C. J. Bruns, C. L. Stern, A. A. Sarjeant, J. F. Stoddart, *J. Am. Chem. Soc.* **2013**, *135*, 183–192; c) J. R  he, M. Rajeevan, K. Shoyama, R. S. Swathi, F. W  rthner, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318451.
- [8] bindfit (Supramolecular, 2020); <http://supramolecular.org>.
- [9] a) S. Feng, L. Wang, B. Mili  n-Medina, A. J. Meixner, M. S. Kwon, S. Y. Park, R. Wannemacher, J. Gierschner, *Adv. Mater.* **2023**, *35*, 2306678; b) H.-J. Kim, P. C. Nandajan, J. Gierschner, S. Y. Park, *Adv. Funct. Mater.* **2018**, *28*, 1705141; c) A. Das, S. Ghosh, *Angew. Chem. Int. Ed.* **2014**, *53*, 2038–2054.
- Manuscript received: June 12, 2024
Accepted manuscript online: July 14, 2024
Version of record online: September 6, 2024