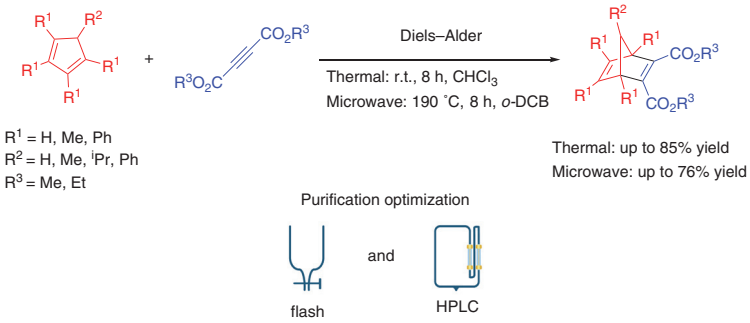
A Practical Synthesis of Multi-Site Functionalized Norbornadiene for Molecular Solar Thermal Energy Storage

A Practical Synthesis of Multi-Site Functionalized Norbornadiene for Molecular Solar Thermal Energy Storage

Monika Shamsabadi[d]
Joost Kimpel[d]
Christian Müller[d]
Kasper Moth-Poulsen*[a,b,c,d]

[a] Catalan Institution for Research & Advanced Studies, ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
[b] Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE EduardMaristany, 10–14, 08019 Barcelona, Spain
[c] The Institute of Materials Science of Barcelona, ICMAB-CSIC, Bellaterra, 08193 Barcelona, Spain
[d] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-41296 Gothenburg, Sweden
Kasper.moth-poulsen@chalmers.se

Published as part of the Cluster *Supramolecular Catalysis and Molecular Switches*



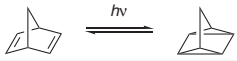
Received: 14.01.2025
Accepted after revision: 24.02.2025
Published online: 17.03.2025 (Accepted Manuscript), 12.06.2025 (Version of Record)
DOI: 10.1055/a-2560-0282; Art ID: ST-2025-01-0021-L

Crowd-Reviewed

Abstract Norbornadienes (NBDs) are promising candidates for molecular solar thermal energy storage (MOST) due to their reversible photoisomerization. A central aspect for future application is the scalable synthesis of NBD derivatives with high solubility. Herein, we report an efficient synthesis and purification of multi-substituted NBDs, achieving diverse substitution patterns and appreciable solubility. The streamlined process for synthesizing and purifying NBDs delivers high yields and purity, which addresses previously significant challenges in NBD-based energy systems. Our findings advance sustainable approaches for MOST through improved NBD stability and usability.

Key words norbornadiene, photoisomerization, functionalization, solubility, renewable energy

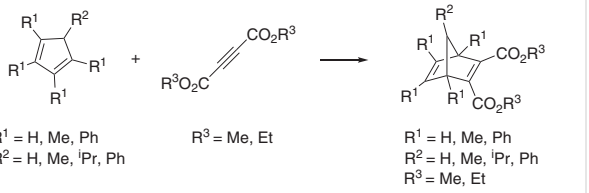
The transition towards sustainable sources of energy necessitates the development of efficient, scalable energy-storage technologies to address the intermittency of renewable sources.[1] While lithium-ion batteries have seen significant advancements, their limitations in energy density, cost, and environmental sustainability have spurred interest in alternative materials and chemical motifs for high-performance energy storage.[2] Organic compounds have emerged as potential candidates for next-generation energy storage materials owing to their tunable properties.[3,4] In particular, norbornadienes (NBDs)[5] have garnered attention due to their unique ability to undergo photoisomerization to highly strained quadricyclanes (QCs) upon irradiation, a process enabling efficient solar energy capture and subsequent thermal energy release (Scheme 1).



Scheme 1 Reversible isomerization of NBDs into QCs

This isomerization is reversible and can be triggered by thermal, catalytic, or light-induced activation, making NBDs ideal for energy-storage systems that require rapid and efficient exothermic release.[6–9] Recent work on photochemical conversion of NBDs has demonstrated promising performance,[10,11] particularly for smaller NBD derivatives that exhibit absorption within the ultraviolet region of the solar spectrum.[12,13]

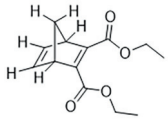
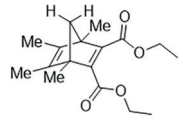
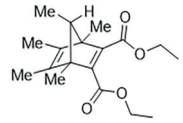
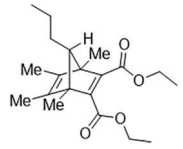
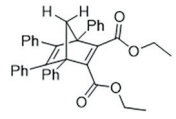
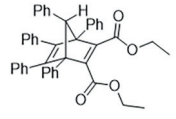
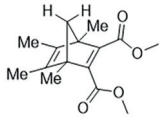
While NBDs show promise, challenges related to solubility and stability must be addressed to fully realize their potential as practical energy-storage materials.[14] Solubility plays a crucial role in the integration of NBDs into energy-storage devices, as the majority of current organic molecular solar thermal storage systems for real-life applications are designed to operate with photoswitches dissolved in a liquid.[15,16] In this work, we explored the synthesis and purification of substituted NBDs, with a focus on improving solubility through the molecular design of NBDs. In conjunction, this study aims to optimize the synthetic protocol and purification techniques while investigating solubility in a system compatible with MOST setups.[17,18]



Scheme 2 General synthesis of substituted norbornadiene

The synthesis of multi-substituted NBDs was achieved through a streamlined, one-step process using commercially available starting materials (Scheme 2). This method enabled functionalization at various sites on the NBD framework to evaluate the effects of the substituents on synthesis, purification, and solubility. A comparative study was performed between traditional thermal synthesis and microwave-assisted synthesis, wherein a substituted cyclopentadiene (CPD) reacted with dialkyl acetylenedicarboxylates—electron-poor dienophiles—*via* a Diels–Alder reaction to yield the target NBDs.

Table 1 Synthesis Parameters and Purification Details for the Synthesized NBDs

Compd	Structure	Thermal synthesis[a]		Microwave synthesis[d]	Purification methods		Relative hydrodynamic volume (Å^3)[e]	
		Solvent	Yield (%)	Yield (%)	Attempted	Successful	NBD	QC
NBD1		$CHCl_3$[b]	0	45	distillation flash chromatography	HPLC	1.071 ± 0.013	1.271 ± 0.025
NBD2		$CHCl_3$[b]	73	10	distillation	flash chromatography HPLC	1.506 ± 0.024	1.447 ± 0.024
NBD3*		$CHCl_3$[b]	60 (0.8:1)	76 (0.8:1)	kugelrohr distillation	flash chromatography HPLC	1.603 ± 0.022	1.585 ± 0.014
NBD4*		$CHCl_3$[b]	83 (1:0.5)	23 (1:0.5)	kugelrohr distillation	flash chromatography HPLC	1.992 ± 0.010	1.965 ± 0.014
NBD5		*o*-DCB[c]	60	35	flash chromatography	HPLC recrystallization	2.785 ± 0.013	2.522 ± 0.017
NBD6		*o*-DCB[c]	0	34	flash chromatography	HPLC recrystallization	2.578 ± 0.040	2.517 ± 0.010
NBD7		$CHCl_3$[b]	85	26	recrystallization	HPLC	1.064	1.000

[a] Reaction conditions: cyclopentadiene (1.00 equiv), dialkyl acetylenedicarboxylate (1.00 equiv), chlorinated solvent (concentration = 12.5 M), 8 h. Yields after purification.
[b] Reaction conducted at 25 °C.
[c] Reaction conducted at 60 °C.
[d] Reaction conditions: cyclopentadiene (1.00 equiv), dialkyl acetylenedicarboxylate (1.00 equiv), *o*-dichlorobenzene (concentration = 8.85 M) at 190 °C. Yields reported after purification.
[e] Determined by smallest enclosing sphere analysis of conformer structures optimized by density functional theory (DFT) using the B3LYP functional at the 6-31+G level of theory. Values are normalized against the smallest hydrodynamic volume of the QC of **NBD7**. Compounds marked with * are reported as mixtures of inseparable isomers, with the isomeric ratios provided where relevant. The isomerism occurs at the bridgehead of the NBD, and the isomers and their ratios are further illustrated in the Supporting Information.

In the thermal synthesis, dialkyl acetylenedicarboxylates were added to the CPD derivative, producing a highly exothermic reaction that persisted for several minutes after the addition of the diene. To minimize photoisomerization of the product to QC, the reaction flask was shielded from light. After 10 minutes, solvent was added as required to evaluate its impact on reaction efficiency. The reaction mixture was stirred for 8 hours and subsequently purified. The microwave-assisted synthesis also involved reacting dialkyl acetylenedicarboxylates with the appropriate CPD precursor. In this case, the reaction was conducted in *o*-dichlorobenzene within a sealed vial at 190 °C, followed by purification (Table 1).

Ester-substituted NBDs exhibit a promising propensity for photoisomerization to QC;[19] however, this behavior complicates structural analysis. The ease of photoisomerization is likely due to the oily nature of these NBDs, in contrast to the greater stability observed in previously reported solid NBDs.[20] The isomerization was evidenced by multiple analytical techniques, including NMR (multiple peaks), and IR spectroscopy (multiple peaks).

A range of work-up techniques for purifying each NBD product was evaluated. Liquid-liquid extraction proved ineffective due to overlapping solubility profiles, while recrystallization was unsuitable for most of the NBDs as these failed to crystallize or co-crystallize possibly due to the many pendant solubilizing groups. Filtration and simple evaporation were also considered, but these methods did not sufficiently remove by-products, particularly those with similar volatilities.

These limitations led to the exploration of more specific techniques such as automated flash chromatography, kugelrohr distillation, and preparatory high-performance liquid chromatography (prep-HPLC) tailored to the unique properties of the NBD derivatives. Purification of the crude product for some NBDs was achieved using flash chromatography with an eluent gradient of 0–20% ethyl acetate in hexanes, yielding the target NBDs following solvent evaporation. Flash chromatography was less effective in eliminating acetylene impurities; however, this was resolved by leaving the sample in an oven at 50 °C for 12 hours.

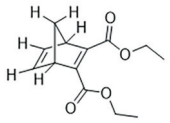
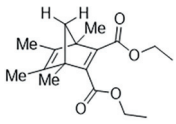
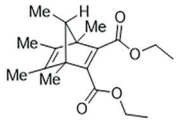
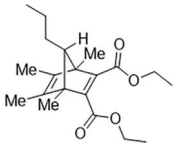
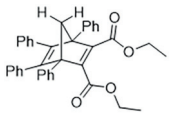
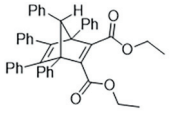
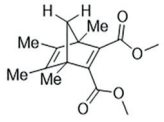
Relative hydrodynamic volumes of the NBD-isomer and QC-isomer for all derivatives were determined by smallest enclosing sphere analysis (see the Supporting Information) of conformers optimized by density functional theory (DFT) (Table 1).[21,22] This was done to assess the feasibility of size-exclusion separation *via* preparatory high-performance liquid chromatography (prep-HPLC). As the NBD changes to the QC, an increase in volume for **NBD1** is observed, whereas a decrease is observed for **NBD2–7**. The changes suggested that prep-HPLC could be used as a suitable purification method. It became the preferred purification technique as it was more effective at separating NBDs from QCs and eliminating acetylene impurities because UV/Vis monitoring allowed for real-time observation of the separation between NBD and QC. This provided a more reliable confirmation of product purity. While prep-HPLC was effective for small-scale purifications, the limited column capacity rendered it impractical for larger quantities. For larger scale purification, kugelrohr distillation was employed. This technique removed residual starting materials due to the low boiling point of alkynes and facilitated the cracking of dimerized, unreacted cyclopentadiene. To ensure the integrity of the purification process, the kugelrohr apparatus was shielded from light.

The solubility of the NBD derivatives was evaluated in two solvents, toluene and anisole, which were selected for their complementary properties. Toluene was chosen for its excellent solvating ability, cost-effectiveness, and previous application in MOST systems. This prevalence as a benchmark solvent also facilitates comparison with previous solubility studies.[10,18,23] Anisole, on the other hand, was selected for its greener profile as a solvent,[24] representing a more sustainable alternative to toluene. This was chosen as an appropriate green alternative since it absorbs in the same UV region as toluene; i.e., it will have no interference in the MOST system. This combination enabled the exploration of both conventional and environmentally conscious options for NBD solubility analysis.

The solubility of NBD derivatives in toluene and anisole showed distinct trends influenced by substituent type and patterns (Table 2). In toluene, NBDs with increasing alkyl chain substitution (**NBD2**, **NBD3**, and **NBD4**) demonstrated significantly enhanced solubility (0.25–0.34 M) compared to minimally substituted **NBD1** (0.12 M) and methoxylated rather than ethoxylated **NBD7** (0.11 M). This trend reflects the role of steric hindrance and hydrophobicity in disrupting intermolecular interactions and promoting solvation. Phenyl-substituted NBDs (**NBD5** and **NBD6**) exhibited moderate solubility in toluene (0.19–0.25 M), underscoring the conclusion that alkyl chains are more effective than planar aromatic groups in enhancing solubility in nonpolar solvents.

Solubility tests in anisole, the greener alternative to toluene, were then explored. The highest solubility was observed for phenyl-substituted **NBD6** (0.60 M), which is almost six times more soluble in anisole compared to toluene. This can be explained by the electron-donating ability of the polar methoxy group on anisole combined with the greater polarizability of aromatic rings on the NBDs. **NBD5** also displayed improved solubility in anisole (0.33 M), further supporting the conclusion that this interaction takes place. In contrast, alkyl-substituted NBDs (**NBD2**, **NBD3**, and **NBD4**) exhibited lower solubility (0.14–0.15 M) reflecting anisole's limited compatibility with hydrophobic alkyl chains. **NBD7**, with its compact and rigid structure, had the lowest solubility in both solvents (0.08–0.11 M). The results

Table 2 Calculated Solubilities of NBDs in Toluene and Anisole

	Structure	Solubility (mol dm^{-3})	
		Toluene	Anisole
NBD1		0.12 ± 0.04	0.09 ± 0.00
NBD2		0.25 ± 0.02	0.15 ± 0.04
NBD3		0.34 ± 0.02	0.15 ± 0.01
NBD4		0.34 ± 0.09	0.14 ± 0.01
NBD5		0.19 ± 0.08	0.33 ± 0.02
NBD6		0.25 ± 0.04	0.60 ± 0.02
NBD7		0.11 ± 0.05	0.08 ± 0.03

underscore anisole's potential as a greener alternative to toluene, particularly for solubilizing phenyl-substituted NBDs.

In conclusion, our findings illustrate the importance of fine-tuning the synthetic methods and purification strategies for substituted NBDs. Moreover, this work highlights that substituent choice significantly affects solubility behavior, with alkyl chains optimizing solubility in toluene and phenyl groups enhancing solubility in anisole. This insight is critical for tuning NBD derivatives for MOST applications, where solvent compatibility and material stability are paramount.

All chemicals, reagents, and solvents were purchased from commercial sources (Fisher, Sigma Aldrich, Merck) and used as received unless otherwise noted. NMR spectra were recorded with a Bruker Avance III HD spectrometer (^{1}H: 800 MHz, ^{13}C: 201 MHz) and Bruker Avance NEO 600 spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz). UV/Vis spectra were measured with an Agilent Technologies Cary 60 UV/Vis spectrometer. IR spectra were recorded with a PerkinElmer Spectrum 3 spectrometer. DSC thermograms were obtained with a Mettler Toledo DSC5+ STARe. HPLC was performed using a LaboACE LC-7080 Plus Series system. Flash chromatography was carried out using a Biotage® Isolera™ System. DFT calculations were performed using the Gaussian 16 and Gauss View 6 packages. High-resolution mass spectrometry was conducted with a Xevo G2-XS QTof mass spectrometer; spectra were obtained using electrospray (ESI) and atmospheric chemical ionization (APCI).

All microwave-assisted syntheses were conducted with a Biotage® Initiator+ Microwave System. Reactions were carried out in 10–20 mL microwave vials within the system's enclosed chamber, which prevented exposure to visible light and protected light-sensitive reactions.

General Procedures

Thermal Synthesis

Cyclopentadiene (7.56 mmol) was gradually added to dialkyl acetylenedicarboxylate (7.56 mmol). The reaction mixture generated a significant amount of heat shortly after the addition of cyclopentadiene, which persisted for several minutes. If the reaction was not performed neat, chloroform (10 mL) was added after 10 min. The mixture was then stirred for 8 h to ensure completion. The crude product was purified using automated flash chromatography with 0–20 % EtOAc in n-hexanes. The resultant NBD fraction was collected and dried in vacuo.

Microwave-Assisted Synthesis

To a solution of dialkyl acetylenedicarboxylate (7.56 mmol) in *o*-dichlorobenzene, cyclopentadiene (7.56 mmol) was added. The microwave vial was sealed and the mixture was heated in a microwave reactor to 190 °C and maintained at this temperature for 8 h. The reaction mixture was then purified by automated flash chromatography with 0–20 % EtOAc in n-hexanes. The resultant NBD fraction was collected and dried in vacuo. The sample was then kept at an oven temperature of 50 °C to remove residual diethyl acetylenedicarboxylate.

NBD 1

Yield: 0.80 g (45%, 3.400 mmol); pale-yellow oil.

IR: 2982 (m, C–H stretch), 2942 (m, C–H stretch), 1705 (s, C=O stretch), 1634 (m, C=C stretch) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.92 (t, *J* = 2.0 Hz, 2 H), 4.23 (q, *J* = 7.2 Hz, 4 H), 3.97–3.88 (m, 2 H), 2.28 (dt, *J* = 6.7, 1.7 Hz, 1 H), 2.08 (dt, *J* = 6.7, 1.5 Hz, 1 H), 1.30 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.28, 152.13, 142.40, 72.87, 60.99, 53.42, 14.12.

HRMS (ESI$^+$, APCI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}O_4$: 259.1127; found 259.1081.

NBD 2

Yield: 0.87 g (73%, 2.984 mmol); pale-yellow oil.

IR: 2983 (m, C–H stretch), 2935 (m, C–H stretch), 1711 (s, C=O stretch), 1615 (m, C=C stretch) cm^{-1}.

^{1}H NMR (800 MHz, CD_3CN): δ = 4.15 (q, *J* = 7.1 Hz, 4 H), 2.04 (d, *J* = 6.4 Hz, 1 H), 1.80 (d, *J* = 6.4 Hz, 1 H), 1.67 (s, 6 H), 1.40 (s, 6 H), 1.23 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (201 MHz, CD_3CN): δ = 165.50, 154.29, 145.21, 77.77, 60.48, 59.73, 13.49, 13.46, 10.60.

HRMS (ESI$^+$, APCI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{24}O_4$: 315.1753; found: 315.1665.

NBD 3

Obtained as an inseparable mixture of isomers (0.8:1).

Yield: 0.86 g (76%, 2.790 mmol); pale-yellow oil.

IR: 2979 (m, C–H stretch), 2934 (m, C–H stretch), 1708 (s, C=O stretch), 1615 (m, C=C stretch) cm^{-1}.

^{1}H NMR (800 MHz, CD_3CN): δ = 4.17–4.10 (m, 4 H), 2.27 (q, *J* = 6.4 Hz, 1 H), 2.11 (d, *J* = 6.4 Hz, 0 H), 1.68 (s, 5 H), 1.63 (s, 5 H), 1.22 (td, *J* = 7.2, 0.8 Hz, 11 H), 0.81 (d, *J* = 6.4 Hz, 2 H), 0.70 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (201 MHz, CD_3CN): δ = 165.86, 165.67, 155.31, 150.95, 146.26, 140.97, 81.42, 80.64, 63.06, 62.81, 60.42, 13.50, 10.89, 10.72, 10.60, 9.25, 9.17.

HRMS (ESI$^+$, APCI$^+$) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{26}O_4$: 329.1909; found: 329.1813.

NBD 4

Obtained as an inseparable mixture of isomers (1:0.5).

Yield: 0.85 g (83%, 2.531 mmol); pale-yellow oil.

IR: 2979 (m, C–H stretch), 2935 (m, C–H stretch), 1708 (s, C=O stretch), 1612 (m, C=C stretch) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.31–4.15 (m, 4 H), 2.51–2.11 (m, 1 H), 1.75–1.62 (m, 6 H), 1.46–1.11 (m, 13 H), 1.01–0.69 (m, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.54–165.30 (m), 156.33–140.86 (m), 86.99, 81.72, 67.90–62.58 (m), 60.48, 28.56–27.11 (m), 22.15–21.01 (m), 18.9, 15.09–13.50 (m), 12.53–10.99 (m), 9.97.

HRMS (ESI$^+$, APCI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{30}O_4$: 357.2222; found 357.2119.

NBD 5

Yield: 0.44 g (60%, 0.810 mmol); white solid; mp 188.70 °C.

IR: 2974 (m, C–H stretch), 1726 (s, C=O stretch), 1710 (s, C=O stretch), 1604 (m, C=C stretch), 1576 (s, C–C aromatics stretch), 1496 (s, C–C aromatics stretch) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.22–7.17 (m, 6 H), 7.14–7.07 (m, 6 H), 7.02–6.98 (m, 4 H), 6.98–6.94 (m, 5 H), 4.28–4.14 (m, 4 H), 3.19 (d, *J* = 6.9 Hz, 1 H), 3.13 (d, *J* = 7.0 Hz, 1 H), 1.20 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.33, 154.73, 153.43, 137.11, 135.43, 129.42, 128.52, 127.72 (d, *J* = 9.1 Hz), 126.74 (d, *J* = 17.7 Hz), 86.51, 79.71, 69.38, 61.15, 13.92.

HRMS (ESI$^+$, APCI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{37}H_{32}O_4$: 541.2379; found 563.2194.

NBD 6

Yield: 0.23 g (34%, 0.380 mmol); white solid; mp 174.85 °C.

IR: 2963 (m, C–H stretch), 1733 (s, C=O stretch), 1716 (s, C=O stretch), 1609 (m, C=C stretch), 1541 (s, C–C aromatics stretch) cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.14 (m, 13 H), 7.08–7.01 (m, 6 H), 6.96–6.93 (m, 2 H), 6.72–6.67 (m, 4 H), 4.55 (s, 1 H), 4.23–4.08 (m, 4 H), 1.15 (t, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.15, 156.45, 150.25, 135.35 (d, *J* = 130.9 Hz), 130.39, 129.85 (d, *J* = 16.8 Hz), 127.79, 127.17 (dd, *J* = 30.9, 20.8 Hz), 126.56, 91.57, 73.15, 61.14, 13.86.

HRMS (ESI$^+$, APCI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{43}H_{36}O_4$: 617.2692; found 639.2497.

NBD 7

Yield: 0.92 g (85%, 3.473 mmol); yellow oil.

IR: 2953 (m, C–H stretch), 2932 (m, C–H stretch), 1714 (s, C=O stretch), 1615 (m, C=C stretch) cm^{-1}.

^{1}H NMR (800 MHz, CD_3CN): δ = 3.68 (s, 6 H), 2.05 (d, *J* = 6.4 Hz, 1 H), 1.80 (d, *J* = 6.4 Hz, 1 H), 1.66 (s, 6 H), 1.39 (s, 6 H).

^{13}C NMR (201 MHz, CD_3CN): δ = 165.96, 154.53, 145.21, 77.82, 59.78, 51.26, 13.45, 10.59.

HRMS (ESI$^+$, APCI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{20}O_4$: 287.1440; found 287.1452.

Solubility determination

NBD (ca. 10 mg) was weighed out into a vial, then solvent (1 mL) was added (final concentration of 10 M) and the vial was vigorously shaken. The mixture was taken up with a syringe and filtered into a pre-weighed glass vial using a PTFE syringe filter (0.22 µm pores). The solvent was removed using a Biotage® V-10 Touch, and the final mass of NBD that passed through the filter was recorded. The same procedure was repeated for each NBD.

The min-max error was calculated by determining the range of measured solubility values for each NBD; that is, Error = (max value – min value)/2.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

The authors acknowledge funding from Göran Gustafssons Stiftelse för Naturvetenskaplig och Medicinsk Forskning, Vetenskapsrådet, and H2020 European Research Council (Grant: 'PHOTHERM'). DFT calculations were enabled by resources provided by Chalmers e-Commons.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-2560-0282.

References

(1) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729.
(2) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J.-M. *Nat. Mater.* **2012**, *11*, 19.
(3) Bren, V. A.; Dubonosov, A. D.; Minkin, V. I.; Chernoivanov, V. A. *Russ. Chem. Rev.* **1991**, *60*, 913.
(4) Quant, M.; Lennartson, A.; Dreos, A.; Kuisma, M.; Erhart, P.; Borjesson, K.; Moth-Poulsen, K. *Chemistry* **2016**, *22*, 13265.
(5) Cristol, S. J. *Tetrahedron* **1986**, *42*, 1617.

(6) Moth-Poulsen, K.; Ćoso, D.; Börjesson, K.; Vinokurov, N.; Meier, S. K.; Majumdar, A.; Vollhardt, K. P. C.; Segalman, R. A. *Energy Environ. Sci.* **2012**, *5*, 8534.
(7) Sun, C. L.; Wang, C.; Boulatov, R. *ChemPhotoChem* **2019**, *3*, 268.
(8) Magson, L.; Hölzel, H.; Aslam, A. S.; Henninger, S.; Munz, G.; Moth-Poulsen, K.; Knaebbeler-Buss, M.; Funes-Ardoiz, I.; Sampedro, D. *ACS Appl. Mater. Interfaces* **2024**, *16*, 7211.
(9) Borne, K. D.; Cooper, J. C.; Ashfold, M. N. R.; Bachmann, J.; Bhattacharyya, S.; Boll, R.; Bonanomi, M.; Bosch, M.; Callegari, C.; Centurion, M.; Coreno, M.; Curchod, B. F. E.; Danailov, M. B.; Demidovich, A.; Di Fraia, M.; Erk, B.; Faccialà, D.; Feifel, R.; Forbes, R. J. G.; Hansen, C. S.; Holland, D. M. P.; Ingle, R. A.; Lindh, R.; Ma, L.; McGhee, H. G.; Muvva, S. B.; Nunes, J. P. F.; Odate, A.; Pathak, S.; Plekan, O.; Prince, K. C.; Rebernik, P.; Rouzée, A.; Rudenko, A.; Simoncig, A.; Squibb, R. J.; Venkatachalam, A. S.; Vozzi, C.; Weber, P. M.; Kirrander, A.; Rolles, D. *Nat. Chem.* **2024**, *16*, 499.
(10) Lorenz, P.; Hirsch, A. *Chem. Eur. J.* **2020**, *26*, 5220.
(11) Zika, W.; Leng, A.; Weiß, R.; Pintér, S.; Schüßlbauer, C. M.; Clark, T.; Hirsch, A.; Guldi, D. M. *Chem. Sci.* **2023**, *14*, 11096.
(12) Schulte, R.; Afflerbach, S.; Ihmels, H. *Eur. J. Org. Chem.* **2023**, *26*, e202201398.
(13) Zähringer, T. J. B.; Perez Lopez, N.; Schulte, R.; Schmitz, M.; Ihmels, H.; Kerzig, C. *Angew. Chem. Int. Ed.* **2025**, *64*, e202414733.
(14) Wang, Z.; Hölzel, H.; Moth-Poulsen, K. *Chem. Soc. Rev.* **2022**, *51*, 7313.
(15) Börjesson, K.; Lennartson, A.; Moth-Poulsen, K. *ACS Sustainable Chem. Eng.* **2013**, *1*, 585.
(16) Dreos, A.; Wang, Z.; Udmark, J.; Ström, A.; Erhart, P.; Börjesson, K.; Nielsen, M. B.; Moth-Poulsen, K. *Adv. Energy Mater.* **2018**, *8*, 1703401.
(17) Hemauer, F.; Steinrück, H.-P.; Papp, C. *ChemPhysChem* **2024**, *25*, e202300806.
(18) Wang, Z.; Hölzel, H.; Fernandez, L.; Aslam, A. S.; Baronas, P.; Orrego-Hernández, J.; Ghasemi, S.; Campoy-Quiles, M.; Moth-Poulsen, K. *Joule* **2024**, *8*, 2607.
(19) Alex, W.; Lorenz, P.; Henkel, C.; Clark, T.; Hirsch, A.; Guldi, D. M. *J. Am. Chem. Soc.* **2022**, *144*, 153.
(20) Orrego-Hernández, J.; Hölzel, H.; Quant, M.; Wang, Z.; Moth-Poulsen, K. *Eur. J. Org. Chem.* **2021**, 5337.
(21) Ritter, J. *An Efficient Bounding Sphere*, In *Graphics Gems*; Glassner, A. S., Ed.; Academic Press: San Diego, **1990**, 301–303.
(22) Liu, P.; Zhang, Y.; Wang, H.; Yip, M. K.; Liu, E. S.; Jin, X. *Computer Aided Geometric Design* **2024**, *111*, 102305 DOI: 10.1016/j.cagd.2024.102305.
(23) Salthouse, R. J.; Moth-Poulsen, K. *J. Mater. Chem. A* **2024**, *12*, 3180.
(24) Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C. R.; Abou-Shehada, S.; Dunn, P. J. *Green Chem.* **2016**, *18*, 288.