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# Norbornadiene-based photoswitches with exceptional combination of solar spectrum match and long term energy storage

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**Abstract:** *Norbornadiene-quadricyclane (NBD-QC) photoswitches are candidates for applications in solar thermal energy storage. Functionally they rely on an intramolecular [2+2] cycloaddition reaction, which couples the $S_0$ landscape on the NBD side to the $S_1$ landscape on the QC side of the reaction and vice-versa. This commonly results in an unfavourable correlation between the first absorption maximum and the barrier for thermal back-conversion. Here, we demonstrate that this correlation can be counteracted by using steric repulsion to hamper the rotational motion of the side groups along the back-conversion path. It is shown that this modification reduces the correlation between the effective back-conversion barrier and the first absorption maximum and also increases the back-conversion entropy. The resulting molecules exhibit exceptionally long half-lives for their metastable forms without significantly affecting other properties, most notably solar spectrum match and storage density.*

Renewable and clean energy sources are a very active research area. As an increasing part of our energy demand is provided from renewables, technologies for storage and load levelling become ever more important in order to compensate for daily and seasonal variations in energy production and demand. In this context, photo-induced energy storage via isomerization reactions in molecules has been proposed as a viable alternative.[1] This process has been referred to as molecular solar thermal (MOST) storage systems[2] or known as solar thermal fuels,[3] and are receiving increasing interest with new molecular designs and device architectures being developed. [4] In these systems, photochromic molecules are converted by irradiation into their respective metastable photoisomers. The energy stored in this fashion can later be released on demand either via thermal or catalytic activation.

Several photochromic motifs, such as tetracarbonyl-fulvalene-diruthenium compounds,[5] azobenzenes,[3,6] norbornadienes[7] and dihydroazulenes[8] have been investigated, both in solution and neat forms,[6d,7l] as well as appended to polymers or integrated onto solid supports.[3,6e] The focus of our group has been on assessing the potential of the norbornadiene (NBD)/ quadricyclane (QC) couple, where light can be used to facilitate a [2+2$\pi$] intramolecular cyclization to form the high energy **QC1** from **NBD1** (Figure 1). It has also been found that the stored energy, which has been measured to be up to 1000 kJ kg$^{-1}$,[7c] can be released by means of a catalyst[7c] or electrochemically.[7j] A set of selection criteria for an optimal MOST system has been formulated, which includes high absorbance of NBD around 500 nm to match the most intense band in the solar spectrum ($h\nu_{abs}$ in Figure 2); high quantum yield ($\Phi$) and a non-conflicting absorbance for the corresponding QC ($h\nu_{abs}^{QC}$ in Figure 2); low molecular weight; high energy difference between NBD and QC isomers; and a high activation energy with high-energy heat release ($\Delta H^{\ddagger}$ in Figure 2), i.e. a stable QC form at ambient temperature implying a long half-life ($t_{1/2}$).

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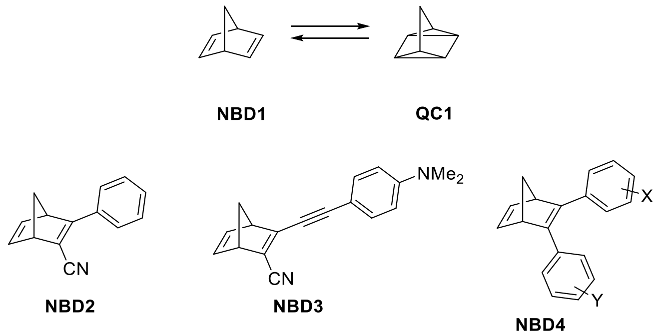

***Figure 1.*** NBD-QC couple **1** and previously synthesised NBD derivatives **NBD2**, **NBD3** and **NBD4** with promising MOST properties.

In practice, MOST designs must be adaptable to different environments. Target storage times, for example, typically vary from a few hours to many months depending on targeted application. It is common when developing MOST systems that one property is improved at the expense of another.[7g] Importantly, in NBD-QC systems the storage time is typically correlated with the first absorption maximum, such that longer storage times come at the expense of a deterioration of the solar spectrum match.[7d,7f,7g,7i] This behaviour can be understood from the coupling of the $S_0$ and $S_1$ energy landscapes (Figure 2). While HOMO and LUMO have π-π and π*+π* character on the NBD side of the reaction, they have σ-σ and σ*+σ* character in the case of QC. The conversion from NBD to QC corresponds to an intramolecular cycloaddition reaction, which involves an avoided crossing of HOMO and LUMO levels. As a result, reducing the $S_0$-$S_1$ spacing for NBD commonly implies a lowering of the barrier for thermal back-conversion ($\Delta H^{\ddagger}$). This detrimental correlation is general and has been observed in the original works by Yoshida, where donor-acceptor molecules red-shifted absorption reduced the energy storage times from months to minutes.[7c,7h] In the work of our group, the introduction of increased donor strength and extended conjugation (molecules **NBD2** vs **NBD3** in Figure 1)[7g] lead to energy storage half-lives of a few hours at room temperature. This trend was also observed for **NBD4** series, using an electronic donor in conjugation with an acceptor (X = donor, Y = acceptor).[7i]

Here, we demonstrate a strategy to effectively counteract this correlation, which involves introducing substituents in the *ortho* position of 2-cyano-3-aryl substituted norbornadienes. We present a series of 17 new norbornadiene and quadricyclane compounds. Four of these bear substituents in the *ortho* position and exhibit an unprecedented increase of a factor of up to two orders of magnitude of the storage lifetime ($t_{1/2}$) as compared to their non-substituted analogues without a deterioration of solar spectrum match or energy storage. Based on experimental evidence and quantum chemical calculations, the decoupling of back-conversion barrier and absorption spectrum is attributed to the effect of steric repulsion on the rotational energy landscape between QC and the saddle point of the transition state (TS). The present approach thus promises to provide a general means for optimizing storage lifetimes without compromising solar spectrum match.

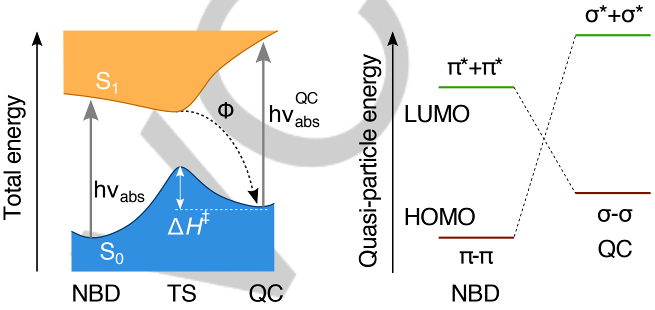

***Figure 2.*** (a) Reaction dynamics for interconversion between NBD and QC. Absorption of a photon leads to activation of NBD from the singlet ground state ($S_0$) to the first excited state ($S_1$). During deexcitation the molecule transforms into its QC form with quantum efficiency Φ. The QC-NBD back-conversion is associated with an energy barrier $\Delta H^{\ddagger}$. (b) The HOMO and LUMO levels on the NBD and QC side of the reaction are related to each other, which implies in general coupling between absorption spectrum and the barrier for back-conversion.

Two approaches were employed in the synthesis of NBD derivatives (full experimental procedures can be found in the SI), one involving a [4+2π] Diels-Alder route, in which by using a literature method suitable dienophiles could be made on a large scale from a host of acetophenones furnishing the set of NBDs shown in Figure 3.[9] In the cases where the initial method did not work, this was supplemented by the reported procedure employing a palladium catalysed Suzuki reaction upon 2-chloro-3-cyanonorbornadiene.[7g] A recent theoretical study showed that certain aromatic donor units could enhance the MOST properties, including dimethylaniline and thiophene, among other electron rich substituents, which were accordingly included in this series.[10] Figure 4 shows the X-ray crystal structure for **NBD2h**, which during the course of this investigation was shown to possess excellent absorption properties (additionally, the structure of **NBD2b** can be found in SI). Large quantities of QCs, which were required for differential scanning calorimetry (DSC) to determine heat release capabilities of these materials, were generated in either chloroform or toluene by irradiation using either a 310 nm or 365 nm. With the exception of **NBD2a** and **2b**, which suffered from inner filter effects, all photoconversions went

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to completion in either toluene or chloroform. Pure samples of **QC2a** and **QC2b** could instead be obtained by column chromatography. Furthermore, in one instance, concentration of a toluene solution of **QC2n** resulted in a rapid partial back conversion thereby furnishing a mixture of NBD and QC forms upon drying. The **NBD2n**/**QC2n** ratio did not seem to change if the mixture was stored at –18 °C for a prolonged period of time.

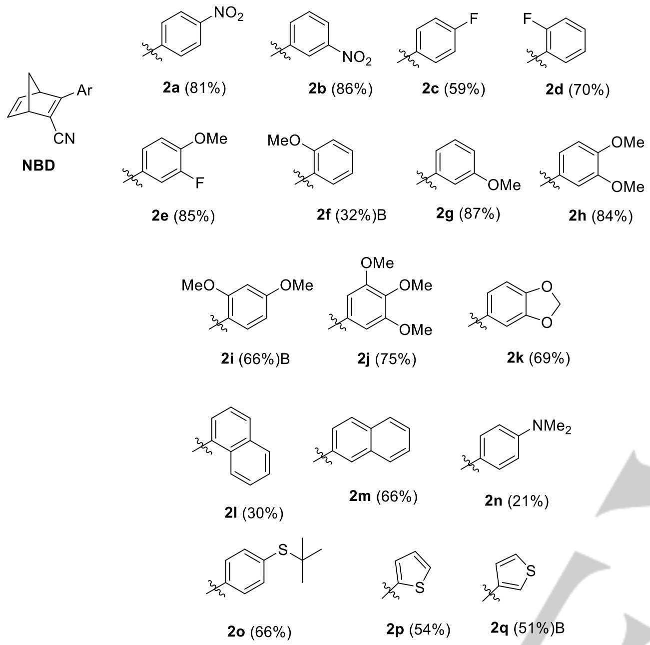

**Figure 3.** NBDs made in this study with yields using the Diels-Alder reaction or via palladium catalysed Suzuki Coupling (highlighted B).

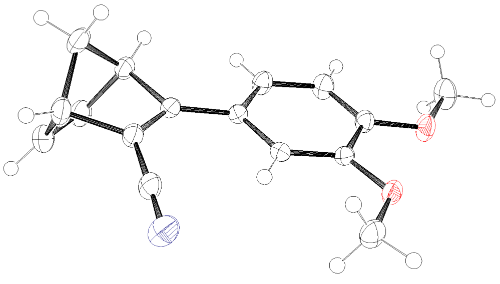

***Figure 4.*** Single X-ray crystal structure of **2h**. Crystals obtained from diethyl ether and *n*-heptane. Ellipsoids are depicted at 50% occupancy. CCDC-1841959 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The absorbance properties for all NBD-QC couples, including the kinetics for the thermal back-conversion were acquired in toluene (Table 1). This allowed for a direct comparison between the new molecules and previously reported **NBD2** and **NBD3**. Corresponding **QC2a-q** were generated *in situ* using a selection of wavelengths, 310 nm, 340 nm, or 365 nm. Here, the spectral window is defined as the offset between the absorption onsets of the respective NBD and QC species. This quantity provides a measure for the efficiency of the absorption during operation and is of fundamental importance when designing practical MOST systems. It was found that the quantum yields of photoisomerisation ($\Phi$) for the nitro-substituted derivatives **NBD2a** and **NBD2b** are rather low compared to all the other derivatives. Compounds with the methoxy donating group in different combinations and even in multiple substitution patterns, show only small variations in absorbance maxima and quantum yields. In many instances, there are, however, large differences between the onsets of absorption for NBDs relative to the corresponding QCs. The highest measured quantum yield of 82% was recorded for the methylenedioxyaryl substituted derivative **NBD2k**, which otherwise has very similar properties as **NBD2h**. The use of naphthalene substituents, **NBD2l** and **NBD2m**, did not seem to enhance the absorption properties for the NBDs. Compound **NBD2n** exhibits the largest red-shift in the UV-vis spectrum, along with a very large extinction coefficient but the optical window of operation was small. While the only structural difference between **NBD2n** and **NBD3** is the absence of the acetylenic linker between the donor and NBD motif, an increase in the quantum yield by more than a factor of two was observed, accompanied by a lowering of the absorbance maximum by 20 nm with a slightly lower extinction coefficient. This difference has previously been shown to be due a better spatial alignment of HOMO and LUMO orbitals in the case of **NBD3**, which leads to a larger transition dipole moment.[7g] The kinetic stability of **QC2a-q** was determined by monitoring the concentration of **NBD2a-q** at three different temperatures (Table 1). For most compounds room temperature half-lives range between hours and at most several weeks and are thus comparable to those of substituted norbornadiene compounds synthesized previously. By contrast unusually high kinetic stabilities were measured for **QC2d**, **QC2f**, **QC2i**, **QC2l** and **QC2m**, which feature room temperature half-lives well on the order of years and/or back-conversion barriers exceeding 130 kJ/mol ($\Delta H^{\ddagger}$, Table 1). Even more strikingly, they feature strongly red-shifted absorption spectra with good solar spectrum match and thus break the correlation between the first absorption maximum and the back-conversion barrier (Figure 5a).

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***Table 1:*** Absorbance properties and kinetic data for the thermal back-conversions for NBD-QC couples **2a-q** at room temperature (298K). Absorbance parameters $\lambda_{max}$, $\lambda_{onset}$ and spectral window are reported in nm. Thermodynamic parameters for thermal back-conversion were determined from the Eyring equation including the Gibbs free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) of activation and half-lives ($t_{½}$ 25 °C).

| | **Photophysical properties** | | | | | **Kinetic data** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **NBD** | | | **QC** | **spectral window** | **$\Delta H^{\ddagger}$ (kJ mol$^{-1}$)** | **$\Delta S^{\ddagger}$ (J mol$^{-1}$K$^{-1}$)** | **$\Delta G^{\ddagger}$ (kJ mol$^{-1}$)** | **$t_{½\ 25\ °C}$ (days)** |
| | **$\lambda_{max}$ (ε x $10^3$)** | **$\lambda_{onset}$** | **Φ (%)** | **$\lambda_{onset}$** | | | | | |
| **2**[5g] | 309 (7.7) | 358 | 58 | 314 | 44 | 112.0 | -1.31 | 112.4 | 54 |
| **3**[5g] | 398 (30) | 456 | 28 | 344 | 112 | 92.5 | -19.1 | 98.2 | 0.204 |
| **2a** | 337 (11) | 401 | 20 | 397 | 4 | 100.9 | -20.9 | 107.1 | 7.74 |
| **2b** | 302 (7.1) | 382 | 19 | 380 | 2 | 117.0 | 11.1 | 113.7 | 108.7 |
| **2c** | 308 (8.3) | 359 | 49 | 307 | 52 | 116.3 | 10.2 | 113.3 | 89.8 |
| **2d** | 301 (6.9) | 350 | 50 | 310 | 40 | 179.9 | 195.5 | 121.6 | 2680 |
| **2e** | 325 (13) | 377 | 40 | 341 | 36 | 111.1 | 0.92 | 110.8 | 33.3 |
| **2f** | 322 (6.5) | 368 | 70 | 339 | 29 | 134.4 | 44.1 | 121.3 | 2273 |
| **2g** | 315 (8.3) | 365 | 60 | 312 | 53 | 116.4 | 11.8 | 112.9 | 78 |
| **2h** | 340 (14) | 389 | 68 | 312 | 77 | 116.2 | 19.4 | 110.4 | 28.7 |
| **2i** | 330 (11) | 385 | 73 | 306 | 79 | 139.4 | 58.7 | 121.9 | 2971 |
| **2j** | 331 (13) | 384 | 68 | 305 | 79 | 109.0 | -3.1 | 109.9 | 24.2 |
| **2k** | 338 (12) | 383 | 82 | 318 | 65 | 106.4 | 8.8 | 103.8 | 1.95 |
| **2l** | 321 (7.6) | 373 | 59 | 325 | 48 | 142.4 | 61.7 | 124.0 | 6729 |
| **2m** | 326 (16) | 384 | 60 | 343 | 41 | 165.8 | 169.0 | 115.4 | 212 |
| **2n** | 374 (23) | 427 | 73 | 401 | 26 | 110.5 | 12.0 | 106.9 | 7.04 |
| **2o** | 324 (12) | 380 | 55 | 300 | 80 | 114.1 | 12.3 | 110.4 | 28.5 |
| **2p** | 336 (11) | 390 | 61 | 353 | 37 | 95.3 | -10.4 | 98.4 | 0.22 |
| **2q** | 312 (9.4) | 367 | 56 | 312 | 55 | 107.8 | -6.7 | 109.8 | 22.7 |

These encouraging features do not compromise the energy storage properties of the compounds as measured using differential scanning calorimetry (SI section 3).

All high-performing derivatives feature a substitution in the *ortho* position of the aromatic substituent, which, as will be explored below, can sterically interfere with the back-conversion reaction. The importance of this steric effect is emphasized by the observation that the compounds (**2c** vs **2d**, **2g** vs **2f**, **2h** vs **2i,** and **2l** vs **2m**) with corresponding or similar *para* substitutions exhibit comparable absorption spectra but much shorter half-lives and smaller back-conversion barriers (**QC2c**, **QC2g**, **QC2j**, **QC2k** and **QC2m**); shaded blue triangles in Figure 5). Comparison of the Eyring plots (SI section 3) as well as the back-conversion enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ shows a qualitative difference between high-performing and "regular" compounds. In fact, the half-lives of QCs with substituents in the *ortho* position were found to be up to two orders of magnitude greater than the aforementioned *para* regioisomers (see SI Figure 5.1 and SI Table 5.2).

To understand this behaviour better we analysed the back-conversion reaction using quantum chemical calculations at the level of density functional theory (DFT); technical details are provided in the SI section 4. While the biradical transition state has a pronounced multi-reference character,[11] computational techniques that can accurately account for this behaviour are computationally very demanding if not impractical for the molecules studied here. Here, we therefore adopt the approach from Jorner *et al.* and approximate the biradical character using unrestricted open-shell DFT.[7b] This approach yields $\Delta H^{\ddagger}$ values in good agreement with experiment and reference CASPT2 calculations for a series of diaryl-substituted NBD compounds investigated earlier (Figure 5b).[7i,11] While it also yields reasonable agreement for the "regular", i.e., non-high-performing, molecules studied here, for several of the high-performing compounds (**QC2d**, **QC2i**, **QC2m**) the calculated and measured barriers are, however, barely correlated (Figure 5b). The difficulties in treating the complexity of the electronic structure of the transition state are a natural source of uncertainty. It is nonetheless possible to extract valuable information pertaining to the mechanisms that give rise to the very long half-lives of the high performers.

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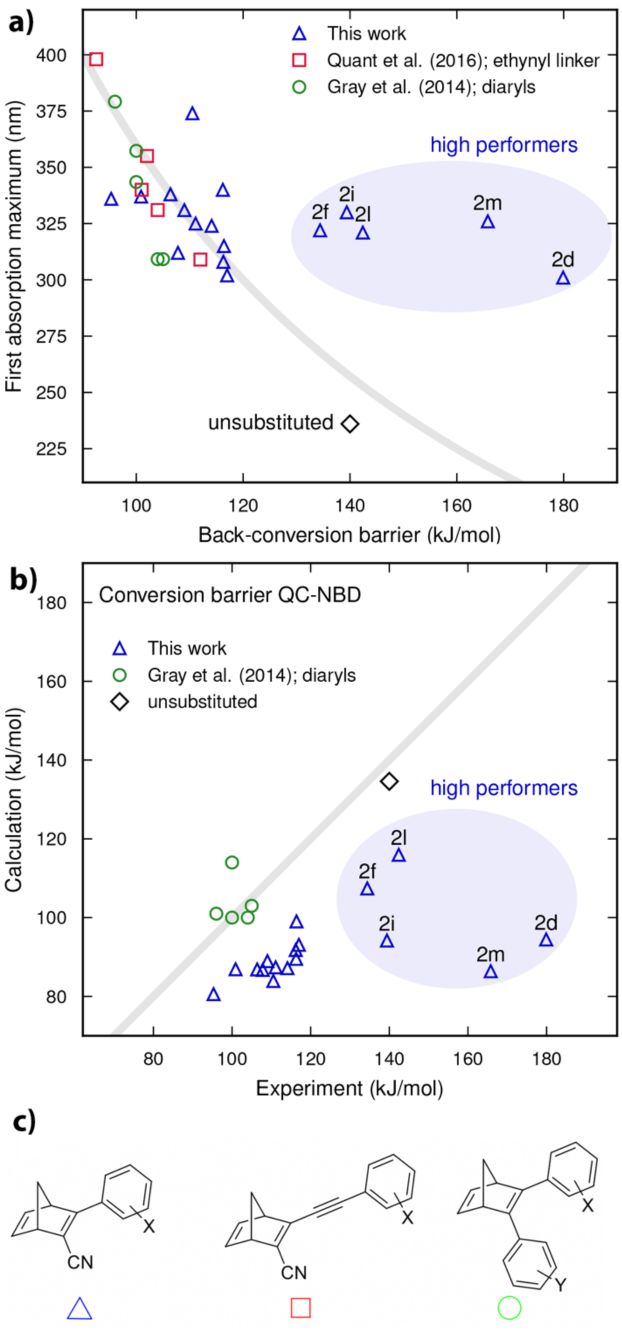

***Figure 5.*** a) Plot of absorption onset for previously reported NBDs and new derivatives against corresponding QC half-lives; b) Plot of theoretical vs. experimental back-conversion barrier; c) molecular structures.

At the level of transition state theory, the rate of QC-NBD conversion is related to the ratio of the partition functions at the initial (QC) and transition states (TS), respectively, where the latter can be approximately decomposed into contributions from vibrational, configurational, and electronic degrees of freedom. To address the former, we computed the vibrational spectrum $\omega_i$ in the QC and TS points of the potential energy landscape (PES), from which we obtained the effective vibrational pre-factor $\omega^{\ddagger} = \Pi_i\, \omega_i^{QC} / \Pi_i\, \omega_i^{TS}$. It is evident from the data in Table 5.2 in the SI that for the high performers **QC2d**, **QC2i** and **QC2m**, $\omega^{\ddagger}$ is at least one order of magnitude larger than for any of the other compounds and, in particular, that $\omega^{\ddagger}$ is substantially increased relative to the respective variants (e.g., **QC2c**, **QC2j**, **QC2k**).

While a comprehensive treatment of the configurational degrees of freedom is computationally very demanding and beyond the scope of this work, further insight can be gained from inspection of the PES associated with rotations of the donor side group with respect to its bond to the parent molecule. Here, comparison of this PES for the pair **QC2c**/**QC2d** (Figure 6) and the series **QC2i**/**QC2j**/**QC2k** reveals that substitution at the *ortho* position has a very pronounced effect on the QC PES, strongly limiting the number of accessible states, whereas its impact at the TS is only modest. The pre-factor (and thus the entropy of back-conversion determined in Table 5.2 in the SI) of the *ortho*-substituted compounds will therefore be enhanced also for configurational reasons relative to their non-*ortho* substituted counterparts.

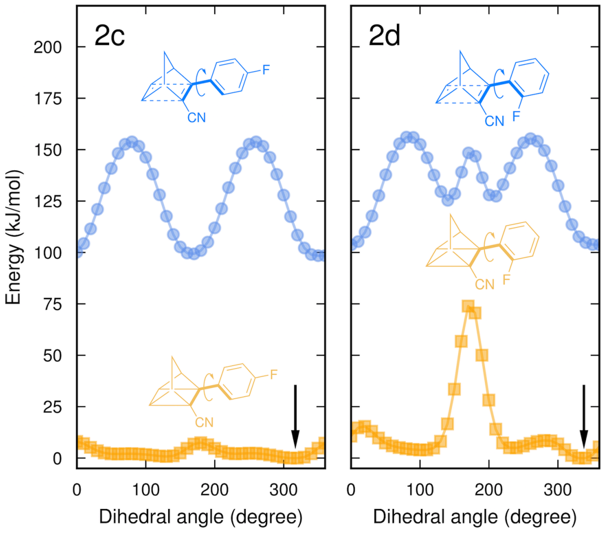

***Figure 6.*** Calculated energy landscapes of the donor side group rotational angle in the QC form (orange squares) and the TS (blue circles) for **2c** (left) and **2d** (right). Substitution in the *ortho* position causes a dramatic change in the QC landscape, but not in the landscape of the TS. The black arrow indicates the minimum energy on the QC landscape.

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In summary the above analysis demonstrates the main factors that contribute to an enhanced half-life. The high-performers developed in this work either feature side groups with substitution on the *ortho* position (**QC2d**, **QC2f**, **QC2i**) or large asymmetric side groups (**QC2l**, **QC2m**). These designs affect the rotational motion of the side group relative to the parent compound, both in terms of the vibrational and configurational degrees of freedom, which modifies the normal correlation between the first excitation energy (i.e., the $S_0$-$S_1$ spacing on the NBD side) and the back-conversion barrier $\Delta H^{\ddagger}$, and gives rise to a larger entropy of back-conversion $\Delta S^{\ddagger}$. This thus provides a rationale that is transferable to other compounds and possibly even other chemical reactions and photoswitch systems. While the present analysis is primarily qualitative in nature, more detailed investigations are warranted to comprehensively explore the back-conversion reaction and to establish the role of the underlying computational techniques, including both the treatment of the electronic structure and the evaluation of the transition rates.

A host of novel 2-cyano-3-aryl substituted NBD derivatives was synthesized using transition metal free catalysis, many of which could be made in multi-gram quantities, in addition to others which required the use of Suzuki protocol. These molecules were comprehensively studied for their utility in MOST applications, including optical properties, thermal conversions and energy storage density. Here, it was found that the *ortho* substituents placed on the benzene ring, or a 1-naphthyl substitution, resulted in the formation of metastable QC with extraordinarily long half-lives at ambient temperature in toluene without incurring reduction of any other properties. To explain how these findings affect the rate of the process, a valuable information we can derive is that the high conformational constrains on the QC energy landscapes forces the reaction pathway from QC to NBD to be topologically more complex and less accessible in the high-performing species compared to the lower performing analogues. This provides a general rationale for the design of compounds that overcome the strong correlation between absorption spectrum and back-conversion rates that have limited the success of compounds developed earlier. The most promising compounds features measured energy densities in the 300–570 kJ/kg, onset of absorption in the 380 nm range combined with energy storage half lives up to 18 years at room temperature. Further research efforts are necessary to push the absorption properties of the NBD beyond 500 nm to better match the solar spectrum.

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**Keywords:** molecular photoswitch • energy storage • energy storage • norbornadiene • quadricyclane • solar energy

[1] W. E. Wentworth, E. Chen, *Solar Energy* **1976**, *18*, 205-214.

[2] K. Moth-Poulsen, D. Ćoso, K. Börjesson, N. Vinokurov, S. Meier, A. Majumdar, K. P. C. Vollhardt, R. A. Segalman, *Energy Env. Sci.* **2012**, *5*, 8534-8537.

[3] T. J. Kucharski, N. Ferralis, A. M. Kolpak, J. O. Zheng, D. G. Nocera, J. C. Grossman, *Nat. Chem.* **2014**, *6*, 441-447.

[4] A. Lennartson, A. Roffey, K. Moth-Poulsen, *Tetrahedron Lett.* **2015,** *56*, 1457-1465.

[5] a) Y. Kinai, V. Srinivasan, S. K. Meier, K. P. C. Vollhardt, J. C. Grossman, *Angew. Chem. Int. Ed.* **2010**, *49*, 8926-8929; b) R. Boese, J. K. Cammack, A. J. Matzger, K. Pflug, W. B. Tolman, K. P. C. Vollhardt, T. W. Weidman, *J. Am. Chem. Soc.* **1997**, *119*, 6757-6773; c) K. Börjesson, D. Ćoso, V. Gray, J. C. Grossman, J. Guan, C. B. Harris, N. Hetkorn, Z. Hou, Y. Kanai, D. Lee, J. P. Lomont, A. Majumdar, S. K. Meier, K. Moth-Poulsen, R. L. Myrabo, S. C. Nguyen, R. A. Segalman, V. Srinivasan, W. B. Tolman, N. Vinokurov, K. P. C. Vollhardt, T. W. Weidman, *Chem. Eur. J.* **2014**, *20*, 15587-15604.

[6] a) G. D. Han, S. S. Park, Y. Liu, D. Zhitomirsky, E. Cho, M. Dincă, J. C. Grossman, *J. Mater. Chem. A* **2016**, *4*, 16157-16165; b) E. N. Cho, D. Zhitomirsky, G. G. D. Han, Y. Liu, J. C. Grossman, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8679-8687; c) W. Feng, S. Li, M. Li, C. Qin, Y. Feng, *J. Mater. Chem. A* **2016**, *4*, 8020-8028; d) K. Masutani, M. Morikawa, N. Kimizuka, *Chem. Commun.* **2014**, *50* 15803-15806; e) Y. Feng, H. Liu, E. Liu, N. Zhao, K. Yoshino, W. Feng, *Sci. Rep.* **2013**, *3*, 3260.

[7] a) A. Ikeda, A. Kameyama, T. Nishikubo, T. Nagai, *Macromolecules* **2001**, *34*, 2728-2734; b) K. Jorner, A. Dreos, R. Emanuelsson, O. E. Bakouri, I. F. Galván, K. Börjesson, F. Feixas, R. Lindh, B. Zietz, K. Moth-Poulsen, H. Ottosson, *J. Mater. Chem. A* **2017**, *5*, 12369-12378; c) V. A. Bren, A. D. Dubonsov, V. I. Minkin, V. A. Chernoivanov, *Russ. Chem. Rev.* **1991**, *60*, 451-469; d) S. Miki, Y. Asako, Z. Yoshida, *Chem. Lett.* **1987**, *16*, 195-198; e) A. D. Dubonsov, V. A. Bren, V. A. Chernoivanov, *Russ. Chem. Rev.* **2002**, *71*, 917-927; f) Z. Yoshida, *J. Photochem.* **1985**, *29*, 27-40; g) M. Quant, A. Lennartson, A. Dreos, K. Moth-Poulsen, *Chem. Eur. J.* **2016**, *22*, 13265-13274; h) Y. Harel, A. W. Adamson, C. Kutal, P. A. Grutsch, K. Yasufuku, *J. Phys. Chem.* **1987**, *91*, 901-904; i) V. Gray, A. Lennartson, P. Ratanalert, K. Börjesson, K. Moth-Poulsen, *Chem. Commun.* **2014**, *50*, 5330-5332; j) O. Brummel, D. Besold, T. Döpper, Y. Wu, S.

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Bochmann, F. Lazzari, F. Waidhas, U. Bauer, P. Bachmann, C. Papp, H-P. Steinrück, A. Görling, J. Libuda, J. Bachmann, *ChemSusChem.* **2016**, *9*, 1424-1432; k) A. Dreos, K. Börjesson, Z. Wang, A. Roffey, Z. Norwood, D. Kushnir, K. Moth-Poulsen, *Energy Environ. Sci.* **2017**, *10*, 728-734; l) A. Dreos, Z. Wang, J. Udmark, A. Ström, P. Erhart, K. Börjesson, M. B. Nielsen, K. Moth-Poulsen, *Adv. Energy Mater* **2018**, *8*, 1703401.

[8] a) Z. Wang, J. Udmark, K. Börjesson, R. Rodrigues, A. Roffey, M. Abrahamsson, M. B. Nielsen, K. Moth-Poulsen, *ChemSusChem*, **2017**, *10*, 3049-3055; b) A. B. Skov, S. L. Broman, A. S. Gertsen, J. Elm, M. Jevric, M. Cacciarini, A. Kadziola, K. V. Mikkelsen, M. B. Nielsen, *Chem. Eur. J.* **2016**, *22*, 14567-14575.

[9] P. K. Sharma, S. Ram, N. Chandak, *Adv. Synth. Catal.* **2016**, *358*, 894-899.

[10] M. J. Kuisma, A. Lundin, K. Moth-Poulsen, P. Hyldgaard, P. Erhart, *ChemSusChem* **2016**, *9*, 1786-1794.

[11] M. J. Kiusma, A. M. Lundin, K. Moth-Poulsen, P. Hyldgaard, P. Erhart, *J. Phys. Chem. C* **2016**, *120*, 3635-3645.

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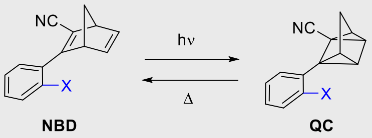
## COMMUNICATION

A series of 2-cyano-3-aryl norbornadienes were synthesized and the properties studied for Molecular Solar Thermal (MOST) energy storage. The quadricyclane isomers with substituents in the *ortho*-position exhibited exceptionally high thermal stability without compromising the other properties. Calculations show a greatly enhanced barrier of rotation in the quadricyclane form coming about from this steric congestion interfering with the transition state.



X ≠ H

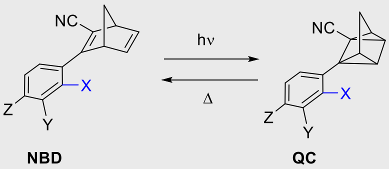
extremely stable QCs

potentially long storage times

*Martyn Jevric, Anne U. Petersen, Mads Mansø, Sandeep K. Singh, Zhihang Wang, Ambra Dreos, Christopher Sumby, Mogens Brøndsted Nielsen, Karl Börjesson, Paul Erhart, and Kasper Moth-Poulsen*

***Page No. – Page No.***

**Norbornadiene-based photoswitches with exceptional combination of solar spectrum match and long term energy storage**



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