

COMMUNICATION

Self-assembled, optically-active {naphthalene diimide}U{cucurbit[8]uril} ensembles in an aqueous environment

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Naphthalene diimides (NDIs) are shown to arrange spontaneously co-facially with cucurbit[8]uril (CB[8]) in an aqueous environment through purely non-covalent interactions. The resultant 2:2 supramolecular complex of NDI and CB[8] is highly fluorescent (>30 times more than the constituent NDIs) due to the formation of NDI-NDI excimers within the supramolecular complex.

1. Introduction

In recent years, molecular recognition has been observed in preorganised macrocyclic systems and cavitands including calixarenes, cyclodextrins (CD), cyclophanes, resorcinarenes and cucurbiturils (CB). Judicious use of these can greatly enhance the diversity, efficiency, selectivity and stability of resultant complexed systems.^{1–3} Cavitands have been shown to bind a range of guests including proteins, small organic drugs and metal ions, creating a wide and versatile range of host-guest assemblies.^{4–9} These systems and overall approach present a myriad of potential applications including as drug delivery hosts and supramolecular catalysts to name but two areas receiving current attention.^{10–12}

Of the various cavitand molecules, CBs present as a versatile and flexible option, not least due to their symmetrical nature and tunability of cavity size with CB[5] to CB[8] and CB[10] so far reported.¹ CBs show preference for guests that are hydrophobic due to their remarkably low polarizability⁹ inside

the cavity, resulting from the absence of functional groups or lone pairs. CB portals, however, are made from ureidyl carbonyls, creating an overall macrocycle that is electrostatically negative at these positions. This manifests in the host-guest interaction or self-assembly showing significant preference to interact with cationic species over neutral and anionic species, forming strong 1:1 complexes in the order of $10^3 - 10^{17} \text{ M}^{-1}$.^{1, 5, 13, 14} CB[8], in particular, is able to form ternary complexes in water with either 1:2 host-guest or 1:1:1 ensembles, creating among these, emissive outputs from heteroternary exciplexes and charge transfer complexes,^{6–8} and homodimers and excimers.^{15–17}

Studies using perylene diimide (PDI) have shown that self-assembly into CB[8] can improve both solubility and increase functionality of the rylene dye, opening up the possibility of rylenes for use in bio-inspired devices.^{18, 19} PDI's smaller, more soluble and synthetically flexible cousin, naphthalene diimide (NDI), is however relatively under explored in CB host-guest systems.^{18, 20} NDIs are well established as versatile molecules for chemical functionalisation.^{21, 22} To increase water solubility, NDIs are commonly functionalised through the imide nitrogen atoms with appropriate hydrophilic groups such as polyethylene glycol, carboxylic acids and tertiary amines.^{23–27}

In their isolated state, non-core-substituted NDIs typically have low to very low fluorescence quantum yields (Φ_f) of a few percent at best, and short fluorescence lifetimes (τ_f) in the range of tens to hundreds of picoseconds,²³ and thus are not commonly used directly as emitting materials. NDIs have, however, been shown to form aggregation-induced emissive (AIE) self-assembled species when stacked co-facially with each other and are finding applications in this regard.^{28–30} The conditions and molecular structural motifs required for AIE from NDIs has been explored to some extent,³¹ however, the

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use of cavitands with NDIs to yield self-assembled emissive species has not been explored.

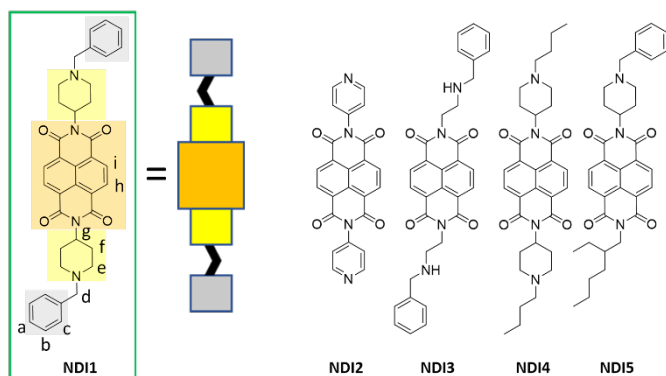


Fig. 1 Molecular structures of **NDI1-5**. The shading on **NDI1** indicates the molecular motifs in the cartoon representation alongside and the lettering a-i denotes the protons assigned to peaks in the ^1H NMR spectra in Fig. 2.

Herein, we undertake a systematic investigation into imide functionalised NDI to form controlled and stable supramolecular emissive species with CB[8] in aqueous environment. The result is the formation of a discrete self-assembled complex wherein two NDIs are held by CB[8] such that a highly fluorescent excimer is formed on photoexcitation purely through non-bonding interactions and preorganisation of the host-guest architecture.

2. Results and discussion

2.1 Design strategy and properties of a fluorescent assembly comprising NDI and CB[8]

The synthesis of **NDI1** (Fig. 1) with rigid 4-amino-*N*-benzylpiperidine moieties at the imides of a non-core-substituted NDI is described in the ESI (S2) and was undertaken with the idea that the piperidinyll nitrogen, when protonated, would induce an ion-dipole interaction with the target CB as well as increase water solubility. Additionally, the benzyl moiety of the 4-amino-*N*-benzylpiperidine bonded to the piperidinyll ring is able to incorporate into CB cavities through hydrophobic effects and should help drive complexation between host and guest. Interestingly, crystals form from an acidic aqueous solution of **NDI1** and CB[8] and the architecture of the constituent **NDI1**•CB[8] complex in the solid state was unambiguously elucidated using X-ray crystallography (ESI, S3).³² The system forms a macromolecular daisy chain structure in which the NDI core does not enter the CB[8] cavity but sits outside allowing for two benzyl groups from two separate **NDI1** molecules to enter the cavity from opposite sides.

To investigate the host-guest interaction between **NDI1** and CB[8] in aqueous solution, ^1H NMR titration experiments were performed in acidified (0.1% TFA) D_2O (Fig. 2). The addition of 1.0 equiv. of CB[8] to a solution of **NDI1** (62 μM) caused: a decrease in intensity of the proton resonance for the benzyl groups (H_{a-c}) at 7.50 ppm and appearance of new upfield signals at 6.25 – 6.75 ppm. These observations are consistent with the

benzyl groups entering the CB[8] cavity and experiencing a changed chemical environment. Upon addition of 1.5 equiv. of CB[8], the proton signal for free benzyl groups completely disappears while the complexed benzyl signals increase in intensity. Interestingly, the piperidinyll proton signals (H_{e-g}) do not significantly shift suggesting that these protons remain outside the CB[8] cavity and that the core of the NDI molecules does not enter the CB cavity. This is consistent with the positive amine groups (they are protonated under the experimental conditions) positioning at the CB carbonyl portals which are overall negative. A similar conclusion regarding NDI not entering the CB cavity was reached by Biedermann et al.,¹⁸ in contrast to their observation of full encapsulation of perylene diimide by CB.

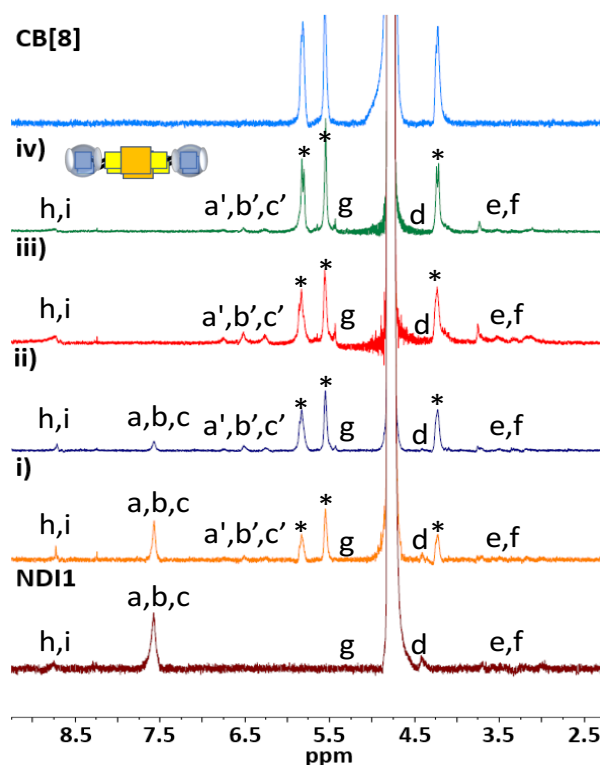


Fig. 2 Partial ^1H NMR spectra (400 MHz, 300 K, 0.1% TFA in D_2O) recorded for **NDI1** (62 μM) in the presence of i) 0.5, ii) 1.0, iii) 1.5 and iv) 2.0 equiv. of CB[8]. Labelling of protons is indicated in Fig. 1. Here, (*) denotes CB[8] proton signals and primes (') denote resonances within the CB[8] cavity. The cartoon in iv) shows the proposed 2:2 complex that forms on addition of CB[8] to **NDI1**.

Accompanying these changes, is a broadening of the naphthalene group signal (H_{h-i}) at 8.62 ppm, and a sharpening of the piperidinyll proton signals (H_{d-g}) on addition of CB[8]. This suggests that the NDIs are in a co-facial, planar arrangement, held by a CB[8] at each end as shown in the cartoon inset to Fig 2. It is well established that π - π stacking usually results in broadening of signals as observed for the naphthalene core due to anisotropy effects, and restricted rotation gives sharp signals as seen for the piperidinyll protons in the ^1H NMR spectrum.^{33, 34} Further evidence that in solution, unlike in the crystal structure, the benzyl groups from two **NDI1** molecules enter the CB[8] cavity from the same side, allowing the **NDI1** molecules to π - π stack, comes from close inspection of the CB[8] proton

signals. Such a binding motif is expected to introduce a splitting in this signal since the chemical environments on either side of the CB[8] are now different, an effect seen previously by Wu and co-workers.^{35, 36} There is splitting visible for the CB protons at 4.29 ppm by the time that 2 equiv. of CB[8] are added, however, the effect is not pronounced. This is likely due to the saturated nature of the piperidinyll ring inducing less of a difference in chemical environment than would an unsaturated ring as seen in the systems studied by Wu and co-workers. Mass spectrometry also supports the proposed binding motif with a 1:1 equiv. solution showing a peak consistent with a species containing two **NDI1** molecules and two CB[8] molecules (ESI, Fig. S4.1). The $[M+2H]^{2+}$ peak at m/z 1942.657 fits well with the calculated value of such a complex of 1942.677.

To investigate and characterise the complexation process and products further, UV-visible and fluorescence emission spectra of 10 μ M solutions of **NDI1** in 0.1% TFA in water were measured neat and with increasing amounts of CB[8]. The absorption (Fig. 3a) and emission profile (Fig. 3b) of **NDI1** in the absence of cavitands show two vibrational modes (363 and 383 nm in absorption and 396 and 414 nm in emission), with such vibronic structure characteristic of non-core substituted NDIs.²¹ Addition of a half molar equiv. of CB[8] has little effect on the absorption spectrum, however, a second half molar equiv. leads to significant changes. The spectrum broadens and maxima shift to lower energy by a few nanometres accompanied by substantial change in the relative strengths of the 0-0 and 0-1 vibrational modes. These perturbations are consistent with self-assembly or aggregate states within similar chromophores *via* π - π stacking^{28, 37} while spectral broadening has been previously attributed to guest electronic levels affected by the CB[8].^{16, 17}

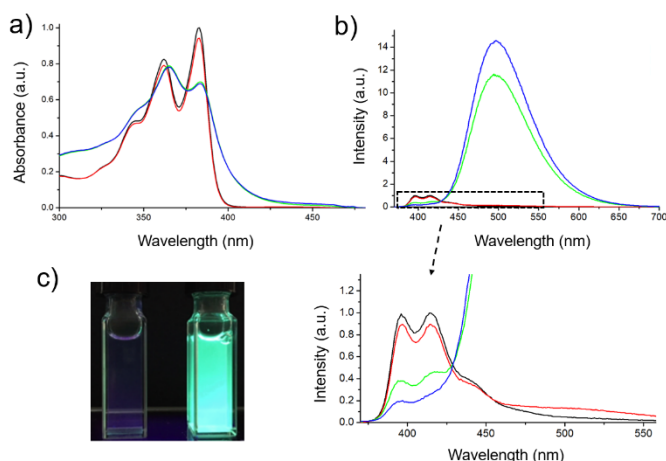


Fig. 3 a) Absorption spectra of **NDI1** in 0.1% TFA in water with half-equimolar titrations of CB[8]. b) Emission spectra ($\lambda_{\text{ex}} = 350$ nm) of 1×10^{-5} M of **NDI1**, in 0.1% TFA in water with half molar equiv. of CB[8], normalised to the maximum emission wavelength (396 nm) of the NDI without CB[8]. Zoom-in area shown below indicated by dashed rectangle. For (a) and (b), CB[8] is 0 equiv. (black), 0.5 equiv. (red), 1.0 equiv. (green) and 1.5 equiv. (blue). c) A solution of **NDI1** alone in acidified water (left cuvette) gives weak violet emission whereas following addition of CB[8] (right cuvette), the solution displays intense cyan emission under UV light ($\lambda_{\text{ex}} = 365$ nm).

On addition of the first half molar equiv. of CB[8], the emission spectrum displays a minor reduction in the characteristic NDI emission bands at 396 and 414 nm, and sees

the emergence of a substantially bathochromically shifted band devoid of vibrational structure. A second half-equiv. of CB[8] leads to a pronounced reduction in emission in the range $\sim 380 - 420$ nm and a multi-fold increase in the intensity of the broad, lower energy band (Fig. 3b). This emission has a maximum at 497 nm and extends to ~ 700 nm, producing a striking and intense cyan colour (Fig. 3c). A third half-equiv. of CB[8] yields more reduction in the higher energy emission and $\sim 15\times$ increase in the lower energy cyan emission. Subsequent aliquots of CB[8] result in only minor changes, indicating that almost all of the **NDI1** molecules have been incorporated into the new emissive complexes. Titration at higher equiv. of CB allows for estimation of the binding constant of the 2:2 **NDI1**•CB[8] complex and is determined to be $1.1 \times 10^5 \text{ M}^{-1}$ (ESI, Fig. S5.1).

A Job's plot (ESI, Fig S6.1) of the change in absorbance as the relative mole fractions of **NDI1** and CB[8] are varied whilst maintaining a constant total concentration ($10 \mu\text{mol L}^{-1}$) shows a maximum at 1:1 mole ratio, consistent with the formation of a 2:2 complex. Further evidence supporting that the unstructured cyan emission originates from NDI excimers comes from the excitation spectrum of **NDI1**•CB[8] measured detecting emission at 500 nm (ESI, Fig. S6.2). The obtained spectrum shows vibrational bands at 349, 366 and 384 nm, similar to the absorption spectrum of the **NDI1**•CB[8] complex (Fig. 3a).

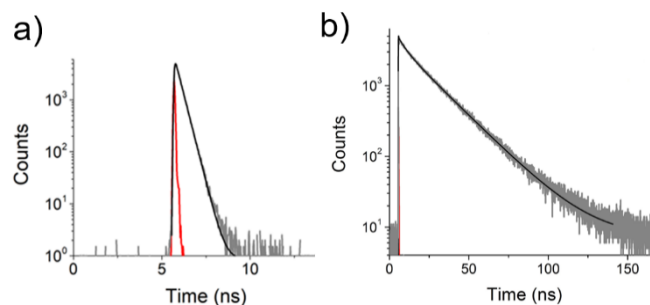


Fig. 4 TCSPC histograms (grey) of **NDI1**, a) without CB[8], emission monitored at 415 nm, and b) with two equiv. of CB[8] monitored at 500 nm. Fitted functions (black) and the IRF (red) also shown. $\lambda_{\text{ex}} = 375$ nm.

Time correlated single photon counting (TCSPC) of **NDI1** (10 μ M) in acidified water shows a short lifetime of 0.38 ns, detecting at 415 nm following excitation at 375 nm (Fig. 4a). Such a short lifetime is consistent with other non-core substituted NDIs due to a fast intersystem crossing mechanism from the singlet excited state to a low lying triplet.^{38,39} Upon addition of 2.0 equiv. of CB[8], much longer lived emission was detected at 500 nm. This emission decays biexponentially with lifetimes of 4.5 ns (25%) and ~ 19 ns (75%) (Fig. 4b). Extended lifetimes similar to these have been observed from other NDI compounds in solution and attributed to excimers.^{40, 41} These take a co-facial arrangement of two NDI molecules similar to the arrangement of the NDIs complexed with CB[8] as inferred by Wu et al.,³⁶ for a range of other aromatic molecules. The presence of two lifetimes in the longer wavelength emission band raises the possibility of there being two emissive species in solution. However, as noted earlier, a Job's plot (ESI, Fig S6.1) shows 1:1 stoichiometry as the mole fractions of **NDI1** and CB[8]

are varied, suggesting that if there are any species in solution aside from the 2:2 complex, they are only present in small amounts, insufficient to be conclusively detected *via* this method. One speculative candidate for a second emissive species is a complex comprising two **NDI1** molecules held co-facially (this being the requirement for an excimer-like emissive species) but at only one end by CB[8].

2.2 Self-assembly of related NDI derivatives with CB[8]

To investigate the self-assembly process further, a series comprising four related NDI compounds was synthesised (Fig. 1), with each member of the series made to elucidate the role of the three key structural components of **NDI1**. To first test the role of the imide substituents as a whole, **NDI2** was synthesised with a pyridine ring appended to each imide position. The

pyridyl nitrogen ($pK_a = 5.25$)⁴² is easily protonated by the acidic conditions of the aqueous solvent, and would be expected to interact with CB[8], however, it is much shorter and cannot enter the CB cavity unless the whole molecule is encapsulated. Titrations of equimolar aliquots of CB[8] into 10 μ M solutions of **NDI2** in 0.1% TFA in water, however, yielded no change in absorption and emission output (ESI, Figs. S6.3 and S6.4). Time-resolved measurements of **NDI2** with show that its fluorescence lifetime is essentially unchanged on addition of CB[8] (ESI, Fig. S7.1). These observations confirm that **NDI2** does not enter the CB[8] cavity and this is consistent with the conclusions drawn earlier that it is the piperidinyl rings and benzyl groups of **NDI1** that are driving self-assembly with CB[8] and not the naphthyl core of **NDI1**.

Table 1 Absorption and emission maxima (λ_{max}), quantum yields (Φ_f) and fluorescence lifetimes (τ_f) of **NDI1-5** in 0.1% TFA in water alone and with two molar equiv. of CB[8].

Entry	Components	λ_{abs} (nm)	ϵ (Lmol ⁻¹ cm ⁻¹)	λ_{em} (nm) ^a	Φ_f^b	τ_{mono} (ns) ^c	τ_{exc1} (ns)	τ_{exc2} (ns)
1	NDI1	383	25,100	390	0.01	0.38	-	-
2	NDI1 •CB[8]	384		500	0.35	-	4.5 (25%)	19.4 (75%)
3	NDI2	381	24,300	392	0.01	0.31		
4	NDI2 •CB[8]	381		392	0.01	0.32	-	-
5	NDI3	382	26,900	392	0.02	0.27	-	-
6	NDI3 •CB[8]	392		404	0.05	1.1	-	-
7	NDI4	383	^d	392	0.01	0.30	-	-
8	NDI4 •CB[8]	383		500	0.03	0.25 (53%)	1.5 (44%)	5.5 (3%)
9	NDI5	385	^d	393	0.02	0.54	-	-
10	NDI5 •CB[8]	385		484	0.05	0.30 (40%)	1.6 (53%)	6.1 (7%)

(a) λ_{ex} = 350 nm for emission spectra. b) Quantum yields for NDI.CB[8] mixtures are for the whole solution under these exact conditions. (c) Fluorescence lifetimes obtained at λ_{em} = 415 nm for solutions without CB[8] and at λ_{em} = 500 nm for solutions with CB[8]. For multi-exponential decays, components are attributed to NDI alone (mono) and to NDI-NDI* excimers (exc) and the % contribution to the initial amplitude of each component is given in brackets. λ_{ex} = 375 nm for all TCSPC measurements. (d) Molar absorptivity of NDIs 4 and 5 could not be determined reliably due to poor solubility

To assess the role of the piperidinyl ring, **NDI3** was synthesised containing *N*-benzyl ethylenediamine moieties at the imide positions. It was anticipated that the distance would still be sufficient for the benzyl group to enter the CB cavity and for the protonated amine group to position near the portal in a similar fashion to **NDI1**. The absorbance and emission spectra of **NDI3** in the absence of CB[8] show maxima at 382 nm and 392 nm (ESI, Figs. S6.5 and 6.6), respectively, as commonly observed in non-core-substituted NDIs. Upon the addition of 2.0 equiv. of CB[8] to the solution of **NDI3**, there is a clear bathochromic shift to 392 nm in the absorption and to 404 nm in the emission spectra consistent with the formation of inclusion complexes.^{17, 43, 44} Notably, these include a 2:2 species as indicated by mass spectrometry (ESI, Fig. S4.2) with a peak seen at m/z 1862.359 which fits well with the calculated value of 1862.614 for $[M+2H]^{2+}$. The emission wavelength shift is accompanied by an increase in intensity, however it remains structured and characteristic of NDI monomer emission. The

observed changes are likely the result of a reduction in non-radiative vibrational depopulation pathways due to complexation with CB[8], rather than the formation of excimers as seen for **NDI1**. TCSPC measurements (ESI, Fig. S7.2) support this with the lifetime of **NDI3** increasing 2.2-fold on addition of CB[8] in line with the increase in area under the emission spectrum. A Job's plot of **NDI3**•CB[8], reveals complexation is occurring with a binding ratio of 1:1 (ESI, Fig. S6.7).

Compounds **NDI4** and **NDI5** provide further insight into the role of each structural component of **NDI1** in the formation of emissive complexes with CB[8]. **NDI4** is an analogue of **NDI1** with the benzyl groups replaced with butyl chains and **NDI5** is a dissymmetric or 'mixed' structure where one *N*-benzylpiperidinyl moiety is replaced by an alkyl group (Fig. 1). Equimolar titration of CB[8] in 1×10^{-5} M solutions of **NDI4** or **NDI5** leads to the formation of a new emitting species upon the

addition of 1.0 equiv. of CB[8] with emission maxima of 502 nm and 483 nm, respectively, (Fig. 5a and 5b).

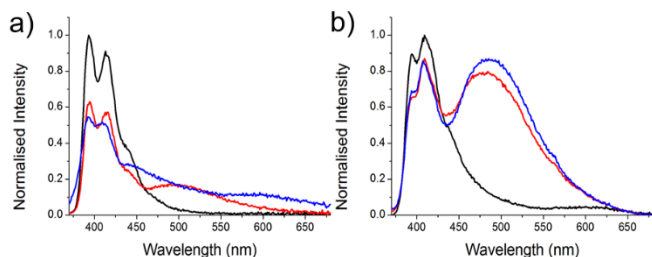


Fig 5. Emission spectra ($\lambda_{\text{ex}} = 350$ nm) of 1×10^{-5} M of a) **NDI4** and b) **NDI5** in 0.1% TFA in water with molar equiv. of CB[8], normalised to the maximum emission wavelength of each NDI without CB[8]. CB[8] is 0 equiv. (black), 1.0 equiv. (red), and 2.0 equiv. (blue).

These emissions show extended lifetimes (ESI, Figs. S7.3 and S7.4) and can be attributed to excimer emission, although the contribution to the total emission is only a few percent and the lifetimes are not as long as for **NDI1**•CB[8]. This suggests that the complexes formed with **NDI4** and **NDI5** are not as stable as **NDI1**•CB[8] consistent with the structural differences between the NDIs, i.e. replacement of both (**NDI4**) or one (**NDI5**) benzyl group with alkyl groups. The addition of a further equivalent of CB[8] does slightly augment the emission from the new species in **NDI5** by ~10% however by this stage in the interaction with CB[8], **NDI4** has begun to aggregate, resulting in weak, unstructured emission in the red part of the spectrum (~600 nm). Due to this aggregation, no further characterisation of the species in solution was undertaken. This highlights that the piperidinyl group is key to holding the NDIs together co-facially, and thus in generating excimer emission. The optical and photophysical properties of the NDI series are summarised in Table 1.

3. Conclusions

In summary, we have exploited a supramolecular approach using cucurbituril (CB[8]) to obtain strongly enhanced emission from an NDI derivative in aqueous solution. Steady-state and time-resolved optical spectroscopies were used to characterise this emission and indicate that it likely arises from an excimer comprising two NDI molecules. This excimer results following optical excitation of **NDI1** in the presence of CB[8] where it forms discrete, self-assembled inclusion complexes. NMR and MS data and results from the study of a series of related NDI molecules suggest that the **NDI1**•CB[8] complexes have 2:2 stoichiometry and that their formation is driven primarily by the benzyl groups at the end of the *N*-imide substituents on **NDI1**. We hypothesise that two NDI molecules enter the cavity of CB[8] from the same side so that they are thereby arranged co-facially and held in place, shackled by the CB[8]s. This positions the positively charged amine group in the *N*-imide substituents adjacent to the CB[8] portals adding further stability to the self-assembled system. The resultant 2:2 supramolecular complex of **NDI1**•CB[8] then yields the enhanced fluorescence emission due to the two NDIs being able to form an excimer following

photoexcitation. This species has spectrally broad emission peaking at ~500 nm, with long lifetimes (~20 ns) and high fluorescence yield (0.35).

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

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32. Crystal data for **NDI1.CB[8]**: $[\text{C}_{86}\text{H}_{86}\text{N}_{36}\text{O}_{20}]^{2+}$. Water and TFA, $a = 14.3621(11)$, $b = 24.1237(15)$, $c = 27.1906(18)$ Å, $\alpha 90$, $\beta 98$, $\gamma 90$, monoclinic, $P2_1/c$, $Z 2$, $V 9328.4(11)$ Å³, $\rho_{\text{calc}} 0.685$ Mg/m³, $F(000)$ 1992, $\lambda 0.71073$ Å, $T 123(2)$ K, $\mu 0.051$ mm⁻¹, Nonius Kappa CCD diffractometer, ϕ and ω scan data, 16404 data collected, 16405 unique reflections ($R_{\text{int}} = 0.0764$) and 16405 observed [$I > 2\sigma(I)$], 640 refined parameters, $R1 0.1325$, $Rw2 0.3384$. Crystallographic data (excluding structure factors) for NDI1.CB[8] have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1860837. Copies of the data can be obtained free of charge on application to the CCDC (email: deposit@ccdc.cam.ac.uk).
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