The synthesis of novel core-substituted naphthalene diimides *via* Suzuki cross-coupling and their properties†

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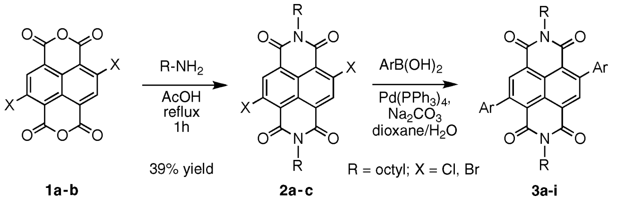
This paper reports the efficient core-substitution of halogenated naphthalene diimides utilizing the Suzuki cross-coupling reaction to install various aryl substituents at the 2,6 positions. The UV-visible spectra of these compounds show a clear absorbance red shift and an enhanced fluorescence output, making them potential candidates for solar-cell dyes and electroactive elements for supramolecular materials.

Naphthalene diimides (NDIs) are compounds of current interest because of their interesting physical and electronic properties with application in OFETs and other optoelectonic devices and in supramolecular chemistry.[1–3] Moreover, core-substituted NDIs, as a subset of this family, display a tunable and highly fluorescent ($\varphi \sim 0.8$) output. Core-substituted NDIs with bathochromically-shifted absorption and emission maxima compared to their unsubstituted counterparts can be achieved by attachment of electron-donating alkylamino and alkyloxy substituents at the 2,6-positions of the NDI core.[4–6]‡ Using this strategy, core-substituted NDIs are finding use in a range of biomimetic and bioinspired systems including electron and energy transfer,[7] artificial photosynthesis,[8] to bridge the 'green gap',[9] n-type organic transistors[10] and formation of conjugated NDI-thiophene polymers[11] and potent G-quadruplex ligands.[12]

In order to utilize NDIs as dyes for solar cell applications, an increased electronic coupling between the naphthyl core and appended electro-active elements is required, while aggregation effects orthogonal to the aromatic plane should be limited to minimise optical 'short-circuiting' based on crystallisation or non-uniformity of thin films. One way of achieving this is to develop a new type of core connectivity that links complementary electroactive elements covalently to the naphthyl core of the NDI.[13,14] In this regard, a few number of core-substituted derivatives with aryl,[13] thiophene,[11b] and cyano[10,13a] groups have been reported. Suzuki coupling of aryl halides with arylboronic acids has served as a powerful reaction for the construction of biaryl units in organic synthesis[15] and may be performed in either organic solvent or biphasic mixtures. We were interested in utilizing this reaction to modify the NDI core and provide some scope by demonstrating a high-yielding synthetic path to novel supramolecular building blocks containing the bi-aryl NDI core.§ In this letter, we report on the efficient synthesis of 2,6-diaryl naphthalene diimides *via* Suzuki cross-coupling (Scheme 1).



Scheme 1 2,6-Diarylnaphthalene diimides formed *via* a Suzuki cross-coupling reaction.

Typically, 2,6-dihalo-substituted NDIs are accessed *via* pyrene chlorination,[5,6] or bromination with dibromoiso-cyanuric acid in hot sulfuric acid, the latter giving 2,6-dibromonaphthalene-1,4:5,8-tetracarboxylic dianhydride **1a** in quantitative yield. The dihalide **1a** was reacted with *n*-octyl amine in hot acetic acid and the resulting NDI **2a** isolated by column chromatography[13b] in 30% yield. The preparation of the dichloro analogue **2b** was achieved using literature methods[5] but is far less desirable, requiring a multi-step synthesis protocol and harmful reagents, such as chlorine gas, to get to **1b**.[1,2]

The scope of these core-functionalisation studies began by first investigating the effect of solvent on the Suzuki cross-coupling efficiency of **2a** with 4-methylphenylboronic acid using Pd(PPh$_3$)$_4$/Na$_2$CO$_3$ (Table 1). The results clearly show that dioxane–H$_2$O (3 : 1) (Table 1, entry 4) is superior to the other aqueous–organic solvent systems tested. With the

Table 1 Effect of solvent on the Suzuki cross-coupling reaction of **2a** with 4-methylphenylboronic acid[a]

Entry	Solvent	Product	Yield (%)[b]
1	Dioxane–H$_2$O (3 : 1)	**3a**	97
2	Dry toluene	**3a**	54
3	Toluene–DMF (3 : 1)	**3a**	70
4	Ethanol–H$_2$O (3 : 1)	**3a**	63

[a] Reaction conditions: **2a** (1.0 mmol), boronic acid (3 mmol), 2 mol% Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$ (1 mL) and dioxane (3 mL), reflux for 12 h under argon atmosphere. [b] Isolated yield.

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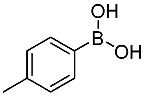
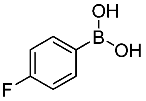
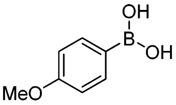
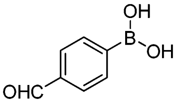
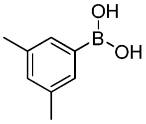
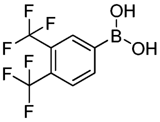
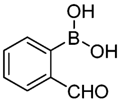
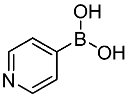
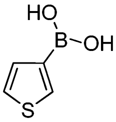
Table 2 Suzuki cross-coupling reaction of **2** with boronic acids[a]

Entry	Ar–B(OH)$_2$	Product	Yield (%)[b]	
			From **2a**	From **2b**
1		**3a**	97	81
2		**3b**	96	78
3		**3c**	93	67
4		**3d**	94	—
5		**3e**	97	—
6		**3f**	95	75
7		**3g**	86	—
8		**3h**	94	—
9		**3i**	96	72

[a] Reaction conditions: **2a** (1.0 mmol), boronic acid (3 mmol), 2 mol% Pd(PPh$_3$)$_4$, 2 M Na$_2$CO$_3$ (1 mL) and dioxane (3 mL), reflux for 12 h under argon atmosphere. [b] Isolated yield.

solvent system in hand, a series of phenylboronic acids were used to extend the scope of the reaction (Table 2) using the dihalides **2a,b**.

The cross-coupling reaction displayed a useful tolerance towards the electronic and steric properties of the boronic acid substrates, yielding the desired 2,6-diaryl substituted products **3a–i** in excellent yields from **2a**. The application of this catalytic system to **2b** with a sample of boronic acids also gives satisfactory yields (67–81%). All of the compounds synthesized are highly soluble in organic solvents and were characterised by ^{1}H and ^{13}C NMR, IR and mass spectrometry.

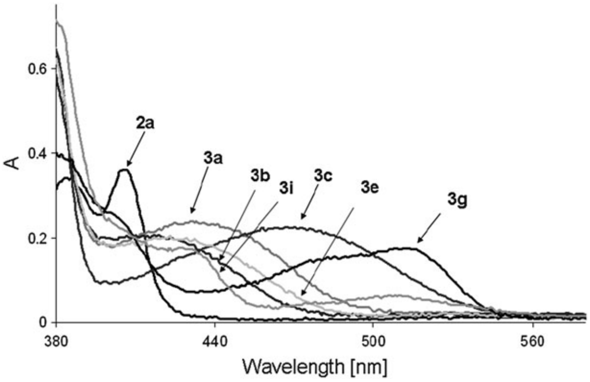


Fig. 1 Absorption spectra of a selection of 2,6-diaryl core-substituted NDIs in CH$_2$Cl$_2$ (concentration = 3 × 10^{-5} M). The spectrum of the parent dihalide **2a** is included for comparison.

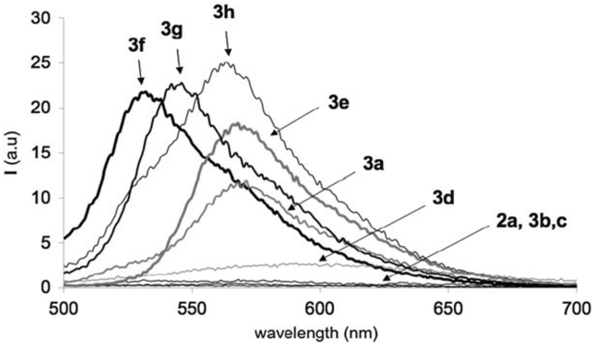


Fig. 2 Emission spectra (λ_{ex} at 377 nm) of core-substituted NDIs (**2a** and **3a–3i**) in CH$_2$Cl$_2$ (concentration = 1 × 10^{-5} M).

We investigated the UV–visible electronic absorption (Fig. 1) and fluorescence (Fig. 2) properties of **3a–i** to assess the spectral variation that the newly installed aromatic substituents impart. The introduction of aryl substituents on the naphthalene core led to significant changes in the absorption spectrum when compared to the unsubstituted naphthalene bisimide **2c** (Scheme 1). The presence of the bromo substituents on the 2,6-positions of naphthalene diimide does not significantly shift the maximum absorption of the π–π* transitions, only affecting the vibronic pattern of the S$_0$-to-S$_1$ transition between 350–400 nm (Fig. 1, Table 3). However, the spectra of core-substituted NDIs become more complex as a result of new vibronic modes being introduced by peripheral substituents.[1–14,16] This is certainly the consequence of a limited, but noticeable, π-conjugation between the naphthalene ring and phenyl core-substituent, leading to a broad transition extending out beyond 500 nm that is dependent on the electronic properties of the aryl substituent.[13]

The introduction of aryl groups with electron-deficient or electron-rich moieties has a pronounced effect on the absorption spectrum, as seen in the cases of **3g** and **3a,c**, respectively (Fig. 1). For all other phenyl substituents investigated we only observe a slight bathochromic shift in absorption spectra (**3b,d,e**) and a moderate band around 500–510 nm in **3f** and **3h** (Table 3).

The fluorescence spectra of the synthesized core-substituted NDIs (**3a–3i**), recorded in CH$_2$Cl$_2$ solution are shown in Fig. 2, and the emission maxima are summarised in Table 3.

Derivatives **3a**, **3e**, **3g** and **3h** are the only fluorescent compounds of the series (Fig. 2), whereas the derivatives of naphthalene substituted with *p*-fluorophenyl (**3b**) and *p*-methoxyphenyl (**3c**) are not fluorescent, and the *p*-formylphenyl compound (**3d**) exhibits only weak fluorescence. Interestingly,

Table 3 Absorption maxima (λ_{abs}), absorption coefficient (ε), emission maxima (λ_{em}) and quantum yield (Φ_{em}) of NDIs in CH_2Cl_2 solution

Compound	λ_{abs}/nm (ε/L mol^{-1} cm^{-1})	λ_{em}/nm	Φ_{em}
2a	377 (43 500), 357 (34 100), 342 (21 150)	385	0.006
3a	433 (9300), 377 (20 900), 359 (17 700), 339 (11 300)	567	0.41
3b	418 (6800), 376 (20 100), 356 (15 600), 334 (9900)	n.d.	—
3c	467 (8400), 378 (20 900), 359 (16 100), 338 (11 000)	n.d.	—
3d	514 (9800), 412 (21 3000), 377 (19 800), 359 (12 600)	n.d.	—
3e	530 (7800), 429 (20 300), 376 (18 500), 357 (14 300), 331 (11 000)	567	0.47
3f	505 (5400), 433 (18 700), 377 (17 900), 359 (12 600), 340 (10 300)	532	0.51
3g	511 (7400), 381 (12 200), 357 (15 400), 321 (23 500)	545	0.58
3h	507 (2300), 429 (8200), 380 (19 400), 360 (17 200).	566	0.62
3i	508 (1140), 432 (5400), 379 (28 300)	n.d.	—

n.d. = not detected due to low emission.

having the formyl group in the *o*-position also leads to fluorescence (see **3g** in Fig. 2). The strong fluorescence for **3a**, **3e**, **3g** and **3h** is increased relative to the NDI **2a** (which experiences a heavy-atom effect), and in some cases is comparable to that of core-substituted NDIs bearing an amine.[16] This underscores the benefit of the carbon–carbon bond on the fluorescence of these compounds and the potential they may have in optoelectronic devices.

Fig. 3 shows three representative cyclic voltammetric responses for the NDIs dissolved in MeCN, and the electrochemical properties of **3a–i** are summarised in Table 4. The electrochemistry of these compounds is characterised by two well-resolved one-electron processes at negative potentials corresponding to the generation of the radical anion and the dianion. In general, both processes are electrochemically reversible; the values of ΔE_p in most cases do not deviate significantly from those expected in organic media. The data in Table 4 also show that the anion and dianion are stable in organic media on the voltammetric timescale, as evidenced by the chemical reversibility of the processes and the peak current ratios ($i_{p,red}/i_{p,ox}$) being close to unity. However, except for **3g** and owing to probable van der Waals contact between the aldehyde and the aromatic ring, we observe that the potentials vary only slightly as a function of the substituents on the aryl group (<250 mV, in spite of the strong variation in the Hammett constant), emphasising that the electronic interaction is weak between the substituents, and that the NDI limits the potential of direct aryl–aryl bonding to tune the electronic properties of the NDI.

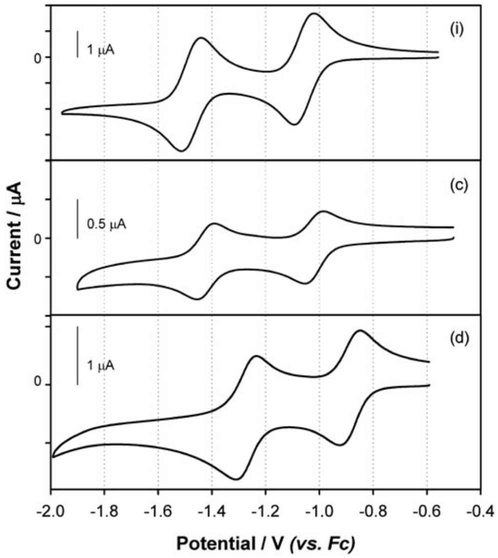


Fig. 3 Cyclic voltammetric responses for (i) **3i**, (c) **3c** and (d) **3d** in MeCN containing 0.1 M $TBAPF_6$ using a 1 mm diameter glassy carbon electrode. The scan rate is 200 mV s^{-1} in each case and the NDI concentrations are 1.2 mM, 0.25 mM and 0.5 mM for **3i**, **3c** and **3d**, respectively.

Table 4 Electrochemical properties of core-substituted NDIs in MeCN (or, for **3e** and **3g**, CH_2Cl_2). The electrolyte was 0.1 M $TBAPF_6$ in each case

	1st reduction			2nd reduction		
Compound	$E°$/V (*vs.* Fc)	ΔE_p/ mV	$i_{p,red}$/ $i_{p,ox}$	ΔE_p/mV	$E°$/V (*vs.* Fc)	$i_{p,red}$/ $i_{p,ox}$
3e	−1.15	75	1.04	−1.55	79	1.00
3i	−1.07	77	0.99	−1.49	76	0.98
3a	−1.05	90	0.98	−1.46	98	0.89
3c	−1.02	74	1.10	−1.42	64	0.98
3b	−0.98	63	0.99	−1.4	70	0.89
3f	−0.92	163	1.18	−1.35	141	1.10
3h	−0.93	93	1.20	−1.34	80	1.25
3d	−0.91	70	1.10	−1.3	63	1.20
3g	−0.68	65	1.21	−0.83	86	1.11

In summary, we have demonstrated an efficient means for core-substitution of 2,6-dihalo-NDIs (X = Br, Cl) by utilizing the Suzuki cross-coupling reaction. The present method allows for the functionalization of NDIs directly on the naphthyl core at the 2- and 6-positions *via* carbon–carbon bond formation. These core-substituted NDIs molecules (**3a–i**) and the facile method by which they may be prepared opens up new opportunities in many applications, including organic dyes, organic field-effect transistors, and in supramolecular self-assemblies. We are currently working on the evaluation of these novel NDIs as n-type field-effect transistors and extending this approach to designing new single-molecule systems capable of long-lived photostable states for labeling applications. The nature of the absorption and fluorescence differences are also under investigation.

Experimental

General remarks

The electrochemical measurements were carried out using a CH instrument model 660C electrochemical workstation

(CH Instruments). Experiments were performed in a small volume (1 mL) electrochemical cell (Cypress systems) using a three-electrode arrangement. This consisted of a 1 mm diameter glassy carbon (GC) disk electrode (Cypress systems), a platinum wire auxiliary electrode and a silver wire quasi-reference electrode. Potentials were referenced to the formal potential of the ferrocene/ferrocenium couple measured *in situ*. The solvent electrolyte system consisted of 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$) (Aldrich, electrochemical grade) in freshly distilled acetonitrile or anhydrous dichloromethane. All scans were conducted at 0.2 V s^{-1} and carried out at ambient temperature (20 ± 2 °C). All solutions were deoxygenated using grade 5 nitrogen prior to electrochemical experimentation. The GC working electrode was polished prior to each experiment using a Buehler Microcloth® polishing cloth with an aqueous slurry of 0.3 μm alumina.

All reagents were purchased from Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the residual CHCl$_3$ peak (7.26 ppm in the ^{1}H NMR and 79.43 ppm in the ^{13}C NMR) and coupling constants (*J*) are reported in Hertz (Hz). Matrix-assisted laser desorption ionisation (MALDI) time-of-flight (TOF) mass spectra were recorded on a Bruker-Dalton Reflex III mass spectrometer.

Typical experimental procedure

A mixture of aqueous 2 M Na$_2$CO$_3$ (1 mL) and dioxane (3 mL) was repeatedly degassed by purging with argon gas, and into it the boronic acid (3 mmol) and *N*,*N*′-di-(*n*-octyl)-2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid diimide **2a** or *N*,*N*′-di-(*n*-octyl)-2,6-dicholoro-1,4,5,8-naphthalenetetracarboxylic acid diimide **2b** (1 mmol) along with 2 mol% of Pd(PPh$_3$)$_4$ was added. The mixture was heated in an argon atmosphere under the complete exclusion of light for 12 h, after which it was quenched with the addition of 10% aqueous HCl. The organic layer was extracted with dichloromethane, washed consecutively with water and brine before being dried over MgSO$_4$ and concentrated. The crude product was then chromatographed over flash silica gel, with DCM–hexane (2 : 1) as eluent to afford core-substituted NDIs (**3a–3i**).

3a: Brown solid, 97% yield. C$_{44}$H$_{50}$N$_2$O$_4$; Mp: 232–233 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.64 (s, 2H), 7.28–7.36 (m, 8H), 4.24 (t, *J* = 6.8 Hz, 4H), 2.47 (s, 6H), 1.59–1.64 (m, 4H), 1.26 (br, m, 20H), 0.86 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 161.8, 152.7, 148.7, 143.5, 141.3, 135.7, 134.6, 133.4, 133.0, 131.6, 129.3, 127.8, 40.0, 30.9, 29.4, 29.3, 27.2, 22.7, 21.3, 14.2. IR (cm^{-1}): 3064, 2969, 2918, 2869, 2214, 1717, 1676, 1560, 1418, 1331, 1216, 769, 715, 689. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 671.3843, found 671.3842 [M + H]$^+$.

3b: Yellow solid, 96% yield. C$_{42}$H$_{44}$F$_2$N$_2$O$_4$; Mp: 211–213 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.62 (s, 2H), 7.42 (d, *J* = 6.93 Hz, 4H), 7.25 (d, *J* = 6.73 Hz, 4H), 4.07 (t, *J* = 6.8 Hz, 4H), 1.65 (m, 4H), 1.26 (br, m, 20H), 0.85 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 162.5, 162.4, 146.9, 136.5, 136.4, 136.0, 130.2, 130.0, 127.5, 125.9, 123.2, 116.0, 115.6, 41.2, 32.1, 31.3, 29.9, 29.8, 29.5, 29.4, 28.2, 27.2, 22.9, 22.8, 14.3, 14.2. IR (cm^{-1}): 3065, 2960, 2925, 2877, 2209, 1714, 1679, 1569, 1427, 1319, 1230, 1214, 762, 719, 687. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 679.3342, found 679.3347 [M + H]$^+$.

3c: Brown solid, 93% yield. C$_{44}$H$_{50}$N$_2$O$_6$; Mp: 245–247 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.64 (s, 2H), 7.52 (d, *J* = 6.69 Hz, 4H), 7.11 (d, *J* = 6.54 Hz, 4H), 4.11 (t, *J* = 6.9 Hz, 4H), 3.90 (s, 6H), 1.66 (m, 4H), 1.29 (br, m, 20H), 0.86 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 162.8, 160.1, 154.1, 149.5, 141.5, 136.3, 132.8, 129.9, 127.4, 125.6, 122.8, 56.0, 31.9, 29.5, 29.4, 27.3, 22.8, 14.2. IR (cm^{-1}): 3062, 2968, 2919, 2872, 2210, 1714, 1668, 1559, 1419, 1327, 1219, 767, 713, 686. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 703.3742, found 703.3739 [M + H]$^+$.

3d: Gray solid, 94% yield. C$_{44}$H$_{46}$N$_2$O$_6$; Mp: 228–229 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 10.14 (s, 2H), 8.63 (s, 2H), 8.07 (d, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 8.2 Hz, 4H), 4.13 (t, *J* = 6.8 Hz, 4H), 1.66 (m, 4H), 1.24 (br, m, 20H), 0.85 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 191.8, 162.3, 162.2, 146.8, 146.6, 136.2, 135.2, 134.9, 134.9, 134.8, 130.8, 129.9, 128.9, 128.4, 128.2, 128.1, 127.6, 126.1, 123.4, 41.3, 31.9, 29.4, 29.3, 27.2, 22.8, 14.2. IR (cm^{-1}): 3062, 2968, 2919, 2872, 2210, 1739, 1717, 1668, 1562, 1417, 1327, 1217, 771, 716, 686. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 699.3429, found 699.3423 [M + H]$^+$.

3e: Light yellow solid, 97% yield. C$_{46}$H$_{54}$N$_2$O$_4$; Mp: 218–220 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 8.62 (s, 2H), 7.12 (s, 2H), 7.01 (s, 4H), 4.05 (t, *J* = 6.8 Hz, 4H), 2.37 (s, 12H), 1.61 (m, 4H), 1.26 (br, m, 20H), 0.86 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 162.8, 162.5, 148.2, 140.8, 138.1, 135.9, 125.9, 125.6, 31.9, 29.9, 29.5, 29.4, 27.2, 22.8, 21.6, 14.2. IR (cm^{-1}): 3063, 2960, 2924, 2879, 2205, 1715, 1681, 1578, 1430, 1319, 1229, 1220, 761, 723, 689. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 699.4156, found 699.4134 [M + H]$^+$.

3f: Gray solid, 95% yield. C$_{46}$H$_{42}$F$_{12}$N$_2$O$_4$; Mp: 205–209 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.63 (s, 2H), 8.03 (s, 2H), 7.80 (s, 4H), 4.23 (t, *J* = 7.1 Hz, 4H), 1.64 (m, 4H), 1.26 (br, m, 20H), 0.85 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 161.9, 151.8, 144.7, 142.3, 135.3, 133.1, 132.4, 131.7, 128.6, 127.7, 162.8, 160.0, 154.1, 149.5, 141.5, 136.3, 132.8, 129.9, 127.4, 125.6, 122.8, 56.0, 31.9, 29.5, 29.4, 27.3, 22.8, 14.2. IR (cm^{-1}): 3062, 2968, 2919, 2872, 2210, 1714, 1668, 1559, 1419, 1327, 1219, 767, 713, 686. MALDI-TOF *m*/*z*: calcd for C$_{44}$H$_{50}$N$_2$O$_6$ 70, 126.49, 126.12, 122.49, 120.69, 41.46, 41.12, 31.93, 29.88, 29. 29, 29.13, 27.16, 22.76, 14.18. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 915.3026, found 915.3026 [M + H]$^+$.

3g: Saffron-coloured solid, 86% yield. C$_{44}$H$_{46}$N$_2$O$_6$; Mp: 234–236 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 10.14 (s, 1H), 10.09 (s, 1H), 8.62 (s, 2H), 8.06–7.85 (m, 4H), 7.56–7.26 (s, 4H), 4.28 (t, *J* = 6.9 Hz, 4H), 1.71 (m, 4H), 1.24 (br, m, 20H), 0.85 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 190.8, 162.8, 162.2, 146.8, 146.2, 136.4, 135.2, 134.9, 134.8, 134.6, 130.5, 129.7, 128.9, 128.6, 128.3, 128.2, 127.7, 126.3, 123.9, 41.8, 31.9, 29.5, 29.4, 27.3, 22.8, 14.2. IR (cm^{-1}): 3062, 2968, 2919, 2872, 2210, 1745, 1714, 1671, 1559, 1419, 1328, 1221, 769, 717, 689. HR-MS (ESI, +ve, DCM/MeOH) *m*/*z*: calcd 699.3429, found 699.3422 [M + H]$^+$.

3h: Brown solid, 94% yield. $C_{40}H_{44}N_4O_4$; Mp: 232–235 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS):δ 8.78 (d, J = 7.6 Hz, 4H), 8.59 (s, 2H), 7.98 (d, J = 7.3 Hz, 4H), 4.09 (t, J = 7.1 Hz, 4H), 1.67 (m, 4H), 1.29 (br, m, 20H), 0.86 (t, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8, 149.5, 147.1, 139.3, 136.4, 135.3, 134.9, 134.9, 134.8, 133.3, 128.8, 128.8, 128.8, 128.1, 128.1, 40.9, 30.9, 29.4, 29.3, 27.3, 22.8, 14.2. IR (cm^{-1}): 3065, 2962, 2921, 2869, 2213, 1714, 1669, 1566, 1419, 1324, 1219, 769, 718, 679. HR-MS (ESI, +ve, DCM/MeOH) m/z: calcd 645.3435, found 645.3437 $[M + H]^+$.

3i: Yellow solid, 96% yield. $C_{38}H_{42}N_2O_4S_2$; Mp: 258–259 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.64 (s, 2H), 7.69 (m, 2H), 7.40 (m, 2H), 6.85 (br, m, 2H). 4.11 (t, J = 6.8 Hz, 4H), 1.66 (m, 4H), 1.27 (br, m, 20H), 0.87 (t, J = 6.8 Hz, 6H). 13C NMR (125 MHz, $CDCl_3$): d 162.8, 156.7, 149.5, 147.1, 144.9, 139.3, 136.6, 136.4, 135.2, 134.9, 134.9, 134.8, 133.3, 129.7, 128.8, 128.8, 128.8, 128.1, 128.1, 127.4, 123.6, 41.2, 31.9, 29.4, 29.3, 27.3, 22.8, 14.2. IR (cm^{-1}): 3065, 2962, 2921, 2869, 2213, 1714, 1669, 1566, 1419, 1324, 1219, 769, 718, 679. HR-MS (ESI, +ve, DCM/MeOH) m/z: calcd 677.2478, found 677.2477 $[M + Na]^+$.

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‡ Similar effects were also observed for 2,3,6,7-tetrasubstituted NDIs; see ref. 17.

§ The aryl coupling (ref. 13) was performed using a Suzuki coupling, though this was less effective. In addition, core-tetrasubstituted NDIs have also been synthesized by cross-coupling reactions; see refs. 13*b* and 13*c*.

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