Supporting Information

for

Efficient bromination of naphthalene dianhydride and microwave assisted synthesis of core-brominated naphthalene diimides

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1. Materials and General Methods: All commercial reagents and solvents were used as received without further purification. Chemicals were acquired from either Sigma-Aldrich Company or TCI America. The 0.1 M KOD in D_2O solution used for ^1H NMR analysis was made from a 0.1 M KOH solution in D2O, with three iterations of fully removing all solvent under reduced pressure and adding equal volume D_2O. NMR spectra of known compounds were collected on a Bruker avance400 400 MHz spectrometer at 25°C. All microwave reactions were carried out in glass pressure sealed tubes (ACE Glass) in an Ethose EX Microwave Extraction System, equipped with a calibrated IR temperature feedback system, form Milestone (model number 134046). Mass spectroscopy data was acquired on an Advion expression Mass Spectrometer. Kinetics were analyzed and empirically modeled for estimated *k* values using the Java simulator Tenua 2.1. DFT calculations were performed with Spartan '08 Parallel for Macintosh on an iMac running OS 10.6.8 with an Intel Core 2 Duo processor.

2. Synthetic Details:

General procedure for brominated NDA mixture enriched in 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride (3). The NDA starting material **1** (2.0g, 7.6 mmol) was added to a solution of fuming sulfuric acid (30% SO_3, 50 mL) in a 250 mL round bottom flask equipped with a stir bar and condenser. The suspension was heated to 50 ˚C for 30 minutes, and then Bromine (1.7 mL, 33 mmol) and a catalytic amount of Iodine were carefully added. The solution was then heated to 100°C and allowed to stir for 36 hr. Aliquots were removed in 6 or 12-hour intervals, precipitated into water and dried before ^1H NMR spectral analysis in 0.10 M KOD. This ensured reaching the optimal reaction point for maximizing the amount of 2 in the product mixture. Upon reaching ~60 mole % of 2 at 36 hr., the solution was allowed to cool to 60 ˚C and carefully poured over ice (500 mL). The resulting yellow precipitate was vacuum filtered, washed with distilled water until neutral, and dried to give giving 3.2 g of a light yellow solid, consisting of

1 (9 %), **2** (10 %), **3** (59 %), **4** (6 %) and **5** (16%). ^{1}H NMR (400 MHz, 0.20 M KOD in D_2O) δ = 7.781 (s, 1H, **2a**), 7.645 (s, 2H, **3a**), 7.623 (s, 1H, **5a**), 7.602 (d, 1H, **2a**), 7.598 (s, 4H, **1a**) 7.443 (d, 1H, **2a**, J = 8.0 Hz), 7.419 (s, 2H, **4a**).

General imidization procedure for dibromo naphthalene diimide 6a. Glacial acetic acid (10 mL) was added to a dry 15-mL glass pressure vial with a Teflon screw cap (Ace Glass) with a typical brominated NDA mixture consisting of 1, 2, 3, 4, and 5 as described above (0.901 g, 2.0 mmol). Octylamine (1.1 g, 8.5 mmol) was then added dropwise to the suspension, and the vial was sealed before being shaken vigorously and then sonicated for 30 minutes at room temperature to ensure a homogeneous mixture. The reaction vessel was then placed in a synthetic microwave with IR temperature feedback (Milestone Ethos EX), and evenly ramped to temperature over 5 minutes to 110°C, where the temperature was held for 20 minutes. The reaction was allowed to slowly cool to room temperature, at which point a pale yellow solid was observed to precipitate from the solution. This precipitate was filtered, washed with glacial acetic acid (3 x 2 mL), and dried to afford 0.72 g of pure dibromo NDI **6a** as a red-orange solid, 91 % of theoretical yield, 55 % overall yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.02 (s, 2H), 4.18 (t, 4H, J = 7.8 Hz), 1.75 (quint, 4H, J = 7.8 Hz), 1.45-1.2 (m, 20H), 0.90 (t, 6H, J = 7.2 Hz). ^{13}C NMR (400 MHz, CDCl3) δ = 160.72, 139.06, 128.94, 128.31, 127.71, 125.32, 124.06, 41.61, 31.44, 27.82, 26.94, 26.82, 26.72, 22.51, 14.00. MS (EI) *m/z* calcd (M), 646.10; found, 646.25.

Dibromo naphthalene diimide 6b. Synthesized using the procedure described above for **6a** to recover 0.71 g of dibromo NDI **6b** as a orange solid, 90 % of theoretical yield, 55 % overall yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.03 (s, 2H), 4.18 (m, 4H), 1.97 (m, 2H), 1.40-1.32 (m, 8H), 0.96-0.91 (m, 12H). ^{13}C NMR (400 MHz, CDCl3) δ = 160.61, 141.23, 130.47, 128.82, 127.55, 125.73, 124.26, 42.18, 35.54, 29.32, 28.43, 27.94, 27.62, 15.51, 14.21. MS (ESI -) *m/z* calcd (M), 646.10; found, 646.51.

Dibromo naphthalene diimide 6c Synthesized using the procedure described above for **6a** to recover 1.34 g of dibromo NDI **6c** as a red solid, 84 % of theoretical yield, % overall yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (s, 2H), 4.05 (t, 4H, *J* = 7.8 Hz), 2.67 (m, 4H), 2.18 (m, 4H), 1.64-1.25 (m, 38H). ^{13}C NMR (400 MHz, *d6*-DMSO) δ = 174.95 162.43, 130.96, 127.71, 127.23, 126.75, 125.12, 123.83, 34.11, 29.39, 29.34, 29.31, 29.25, 29.19, 29.00, 28.94, 27.42, 26.21, 24.95. HRMS (ESI +) *m/z* calcd (M + Na), 841.1675; found, 841.1677.

Dibromo naphthalene diimide 6d Synthesized using the procedure described above for **6a.** The crude filtration product was further purified via column chromatography using dichloromethane as the eluting solvent to recover 0.57 g of dibromo NDI **6d** as a purple solid, 71 % of theoretical yield, 42 % overall yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.02 (s, 2H), 4.18 (t, 4H, *J* = 7.8 Hz), 1.75 (quint, 4H, *J* = 7.8 Hz), 1.45-1.2 (m, 20H), 0.90 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (400 MHz, CDCl3) δ = 160.72, 139.06, 128.94, 128.31, 127.71, 125.32, 124.06, 41.61, 31.44, 27.82, 26.94, 26.82, 26.72, 22.51, 14.00. HRMS (ESI +) *m/z* calcd (M + Na), 711.0291; found, 711.0290.

^{1}H NMR Spectra.

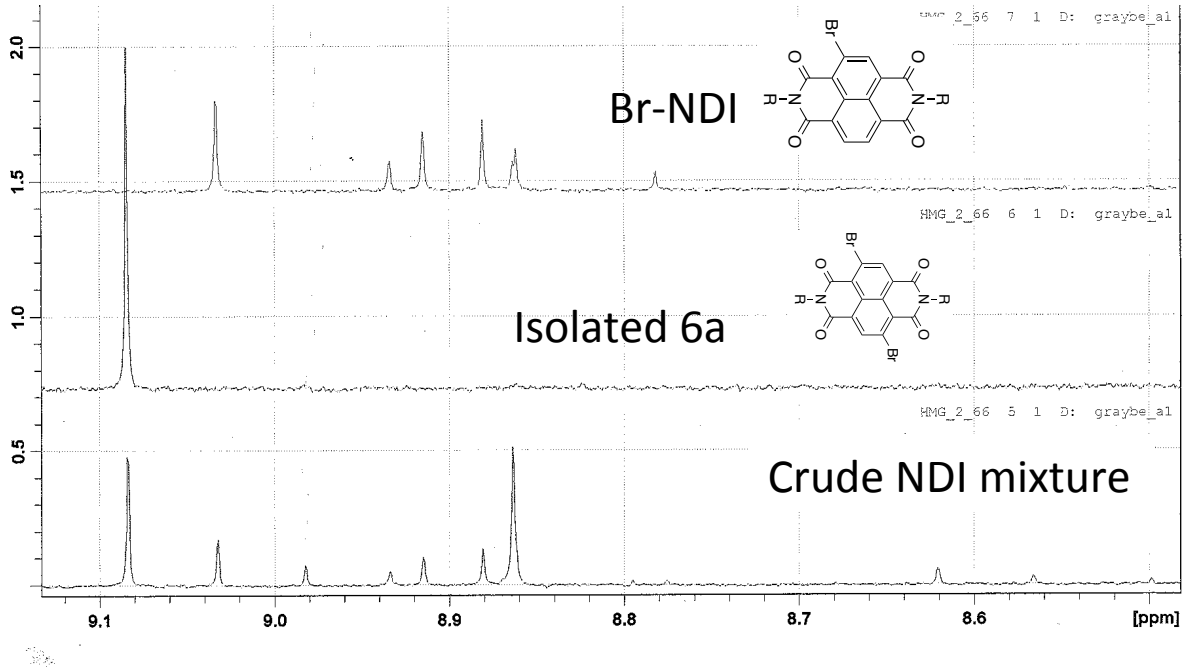

Figure S1. 400 MHz ^{1}H NMR spectrum in $CDCl_3$ of a crude mixture of **6a**, overlaid with the pure filtered **6a** and also showing the corresponding purified Br-NDI.

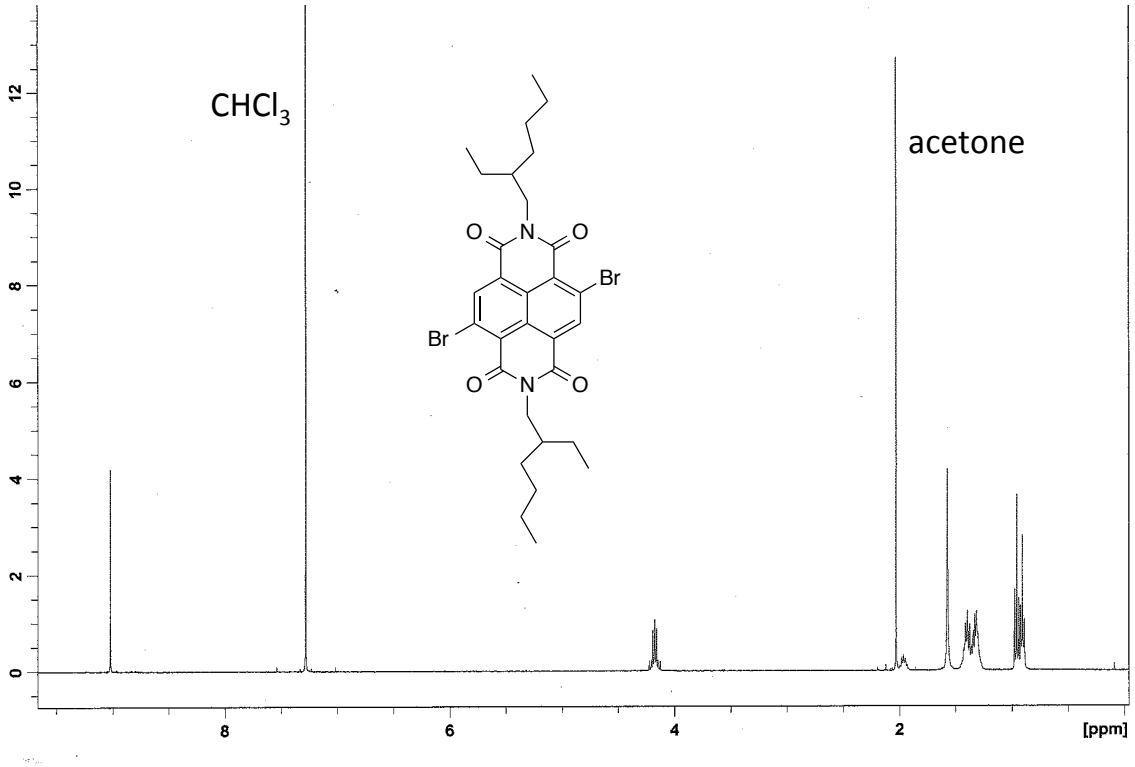

Figure S2. 400 MHz ^{1}H NMR of **6b** in $CDCl_3$.

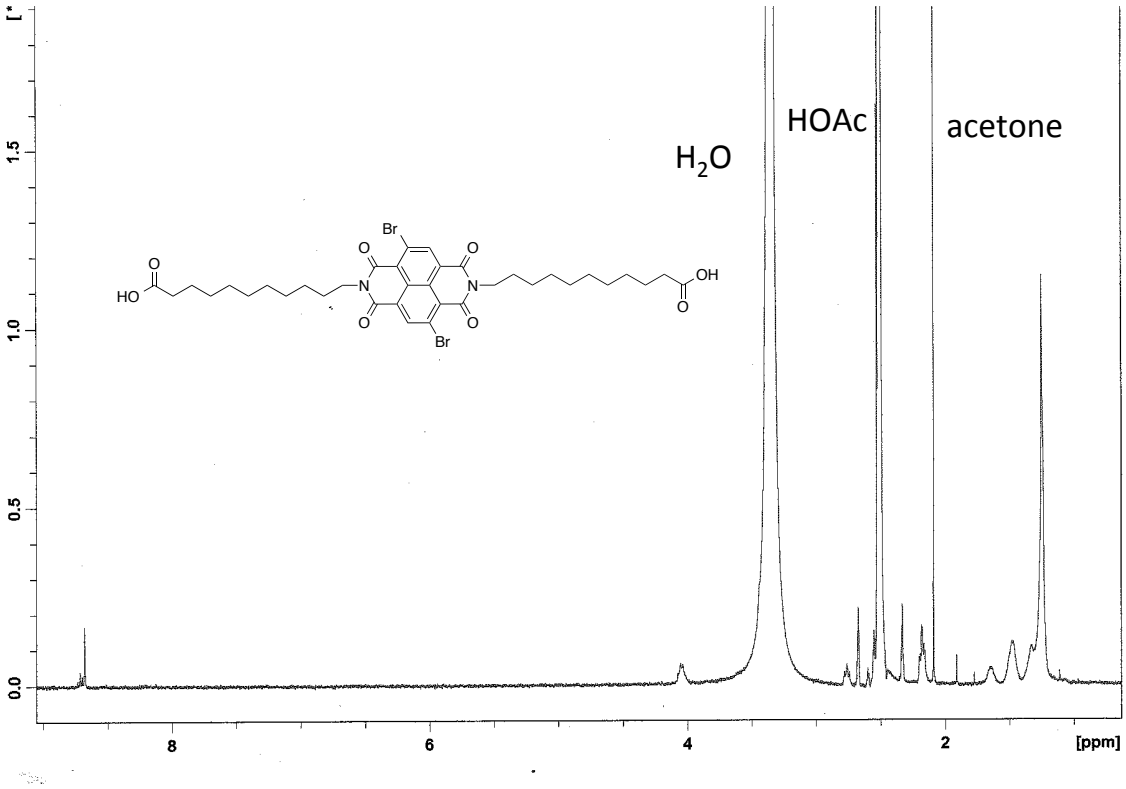

Figure S3. 400 MHz ^{1}H NMR of **6c** in *d6*-DMSO**.** Peak broadening due to aggregation in NMR solvent.

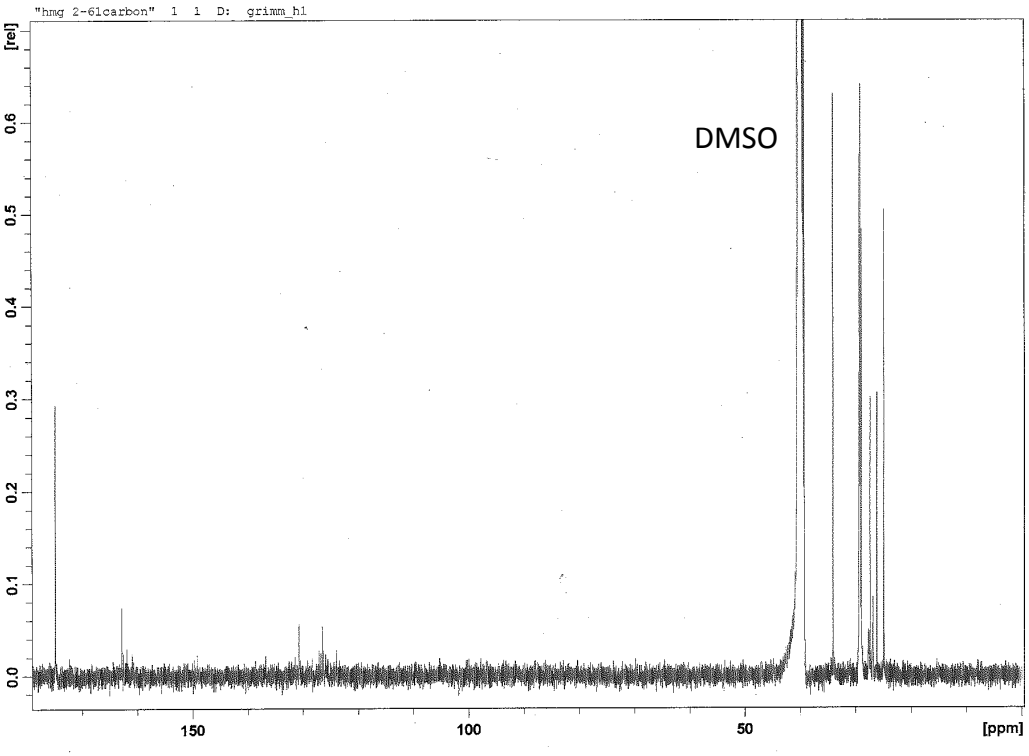

Figure S4. 400 MHz ^{13}C NMR of **6c** in *d6*-DMSO**.** Aggregation leads to low intensity of aromatic carbons.

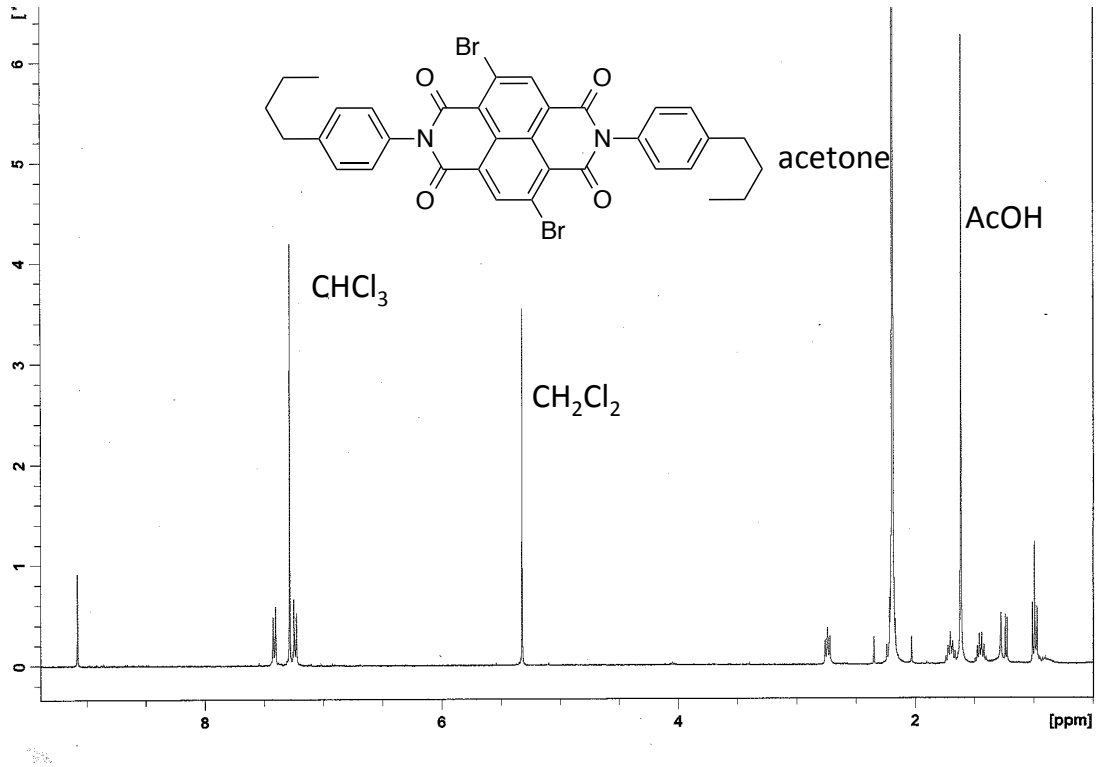

Figure S5. 400 MHz ^{1}H NMR spectrum of **6d** in $CDCl_3$.

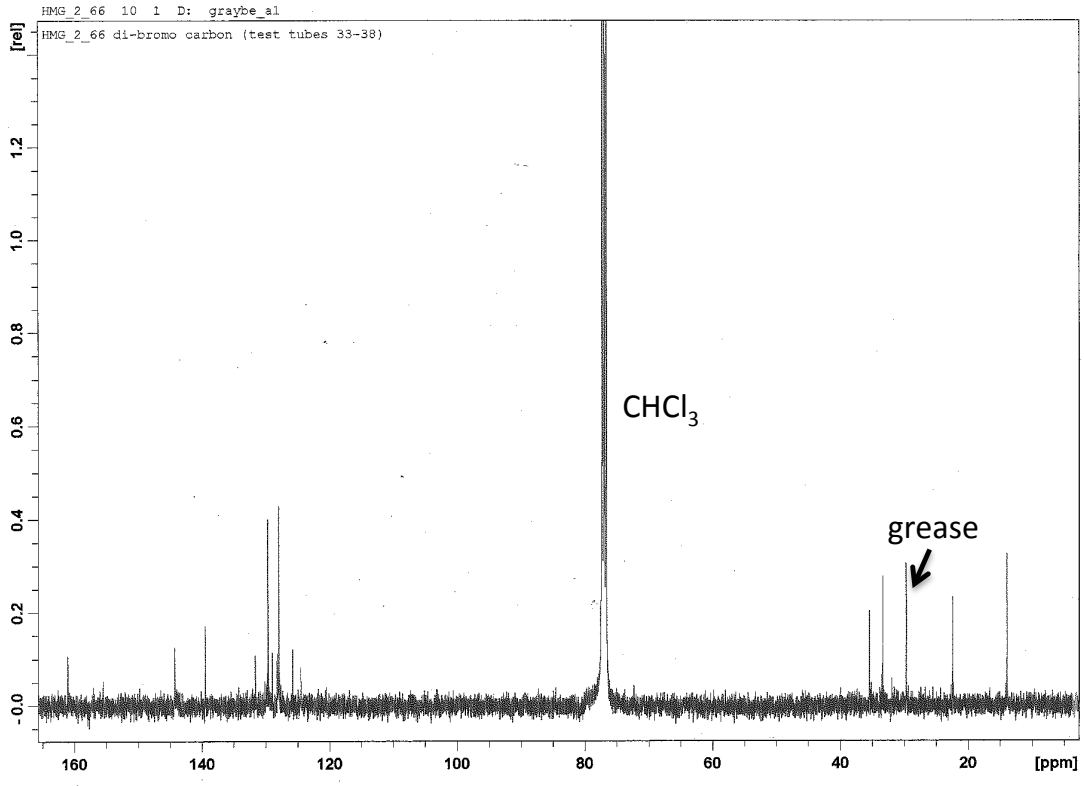

Figure S6. 400 MHz ^{13}C NMR of **6d** in $CDCl_3$**.** Aggregation leads to low intensity of aromatic carbons.