Electronic Supplementary Information

Solvent-induced multicolour fluorescence of amino-substituted 2,3naphthalimides studied by fluorescence and transient absorption measurements

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Experimental

General methods

¹H and ¹³C NMR spectra were collected either on VARIAN Mercury 300 (300 MHz), VARIAN 400MR (400 MHz) or VARIAN NMR System 600 (600 MHz) spectrometers. IR spectra were measured using a SHIMADZU IR Prestige-21 spectrophotometer. Elemental analyses were performed using Perkin-Elmer 2400II at the Micro Elemental Analysis Laboratory of Okayama University.

Steady state absorption spectra were recorded on JASCO U-best 50 or JASCO V-530 spectrophotometers. Fluorescence and phosphorescence emission spectra were obtained on a Hitachi F-7000 spectrophotometer and were not corrected. Fluorescence excitation spectra were recorded on a JASCO 5300 spectrophotometer using a 1-cm path-length quartz cell at room temperature under aerated conditions, and corrected against the instrumental response by using rhodamin B as the standard. Spectroscopic grade solvents were used for the absorption and the fluorescence measurements.

The fluorescence quantum yields were obtained with a Hamamatsu Photonics C9920-02 absolute PL quantum yields measurement system using argon-purged sample solutions. Fluorescence lifetimes (τ_F) were determined with a Hamamatsu Photonics Tau time-correlated single-photon counting fluorimeter system.

Transient absorption measurements

Third harmonics (355 nm) from a Nd:YAG laser system (12 mJ / pulse, Lotis-TII, LT-2137) and 400 nm (7 mJ / pulse) laser pulses from a Ti:Sapphire laser system (Lotis-TII, LT-2211) pumped with second harmonics (532 nm) from the Nd:YAG laser system were used as the excitation laser light sources. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.^{S1} Transient absorption spectra were obtained using a Unisoku USP-T1000-MLT system, which provides a transient absorption spectrum with one laser pulse. The obtained transient spectral data were analyzed using the least-squares best-fitting method. The temporal data of absorbance changes were analyzed by using the least-squares best-fitting method. The sample solutions were deaerated by Arbubbling.

Theoretical calculations

Theoretical calculations were performed by using GAUSSIAN 09 Revision C. 01 package^{S2} The molecular geometries of **1ANI**, **5ANI**, and **6ANI** were optimized at the B3LYP/6-31G+(d)

level. Electronic transitions were calculated with the optimized structures by TD-DFT method at the TD-B3LYP/6-31G+(d) level of theory in vacuum.

Materials

2-(p-Toluenesulfonylmethyl)benzonitrile



A mixture of 2-(Bromomethyl)benzonitrile (2.79 g, 14.2 mmol), sodium *p*-toluenesulfinate (2.68 g, 15.0 mmol) Bu₄NBr (0.24 g, 0.72 mmol) in 1,2-dimethoxyethane (DME, 18 ml) was stirred at r.t. for 20 h. H₂O (70 ml) was added to the mixture. The resulting mixture was stored in a refrigerator and the precipitate formed was collected and dried under vacuum to afford 2-(*p*-toluenesulfonylmethyl)benzonitrile as colorless solid (3.77 g, 98 %), mp 164–166°C (lit. $158-160^{\circ}C)^{S3}$.

¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ = 2.44 (s, 3H), 4.55 (s, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.43–7.49 (m, 1H), 7.55–7.64 (m, 5H). IR (neat) $v_{\rm max}$ 1146 (S=O), 1236 (S=O), 2226 (CN).

Dimethyl 1-amino-2,3-naphthalene dicarboxylate 1^{S4}



A solution of 2-(*p*-Toluenesulfonylmethyl)benzonitrile (3.50 g, 12.9 mmol) and dimethylfumalate (2.78 g, 19.3 mmol) in dimethoxyethane (DME, 80 ml) was dropwise added to a suspension of NaH (60% in oil, 2.32 g, 38.6 mmol) in DME (50 ml). The mixture was stirred at r.t. for 3 h, then refluxed overnight. The resulting mixture was diluted with CH_2Cl_2 (200 ml), and washed with water. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was chromatographed on silica gel using a hexane : AcOEt (1 : 1) containing 1% NEt₃. The crude product obtained was further purified by silica gel chromatography eluting with hexane then AcOEt to afford compound **1** as yellow solid 2.35 g (70 %), mp 70–73°C (lit. 75–76°C).^{S5}

¹H NMR (600 MHz , CDCl₃) $\delta_{\rm H}$ = 3.87 (s, 3H), 3.90 (s, 3H), 6.36 (br, 2H), 7.38 (s, 1H), 7.53–7.56 (ddd, *J* = 1.5, 6.9, 8.4 Hz, 1H), 7.57–7.60 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H).

1-Amino-2,3-naphthalenedicarboxylic acid



To a solution of 1-amino-2,3-naphthalene dicarboxylate (1.62 g, 6.25 mmol) in THF (90 ml) was added an aqueous solution of LiOH^{S6} (2.5 M, 50 ml). The solution was stirred at 80°C for 43 h. The insoluble materials were filtered of and washed with Et₂O. The filtrate and washings were combined and extracted with water (200 ml). The aqueous layer was acidified (pH~3) with 6M HCl and extracted with AcOEt (200 ml). The extract was washed with water, dried (MgSO₄) and concentrated under reduce pressure. The residue was washed with CHCl₃ to afford 1-amino-2,3-naphthalenedicarboxylic acid 1.44 g (99.8 %), mp >130°C (dec). The crude product was used in the next step without further purification because of difficulty of purification by chromatography.

¹H NMR (600 MHz, (CD₃)₂CO) $\delta_{\rm H}$ = 7.53 (s, 1H), 7.62–7.64 (ddd, *J* = 1.2, 7.2, 8.4 Hz, 1H), 7.70–7.73 (ddd, *J* = 1.2, 7.2, 8.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H). ¹³C NMR (150 MHz, (CD₃)₂CO) $\delta_{\rm C}$ = 105.6, 120.4, 123.8, 124.6, 128.1, 130.0, 130.7, 133.2, 136.2, 145.9, 162.4, 169.8. IR (neat) $v_{\rm max}$ 1611 (C=O), 1649 (NH₂), 2504, 2816 (OH), 3466, 3393 (NH₂) cm⁻¹.

1-Amino-2,3-naphthalene dicarboxylic anhydride (2)



Solid 1-amino-2,3-naphthalenedicarboxylic acid (30 mg, 0.13 mmol) was heated at 130°C under in vacuum (0.02 MPa). After the color of the solid turned yellow, the solid was cooled to r.t. and recrystallized from an acetone-CHCl₃ mixture to afford anhydride **2** (23.5 mg, 85 %), mp > 300°C. ¹H NMR (600 MHz, acetone- d_6) $\delta_H = 7.27$ (br, 2H), 7.76–7.79 (ddd, J = 1.2, 6.9, 8.4 Hz, 1H), 7.79 (s, 1H), 7.81–7.83 (ddd, J = 1.2, 6.9, 8.0 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H). ¹³C NMR (150 MHz, acetone- d_6) $\delta_C = 101.6, 116.1, 124.6, 126.4, 127.7, 129.4, 131.3, 132.1, 138.3, 148.3, 164.7, 165.6. IR (neat) <math>v_{\text{max}} 1744, 1802$ (C=O), 3385, 3481 (NH₂) cm⁻¹. HRMS (ESI, *m/z*) Calcd for C₁₂H₇NNaO₃ [M+Na]⁺ 236.0318. Found 236.0335.

N-Propyl-1-aminonaphthalene-2,3-dicarboxyimide (1ANI)



To a solution of anhydride **2** (0.10 g, 0.47 mmol) in AcOH (20 ml) was dropwise added propylamine (0.83 g, 1.41 mmol). The reaction mixture was refluxed for 6 h. The resulting mixture was diluted with CHCl₃ (100 ml) and successively washed with water and 10% K₂CO₃ aq. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on silica gel (Hexane : AcOEt = 3 : 1) to afford **1ANI** 88.4 mg (74 %). Yellow crystals, mp 187–188°C. ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ = 0.97 (t, *J* = 7.2 Hz, 3H), 1,73 (sext, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 6.02 (br, 2H), 7.62–7.66 (m, 2H), 7.67 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) $\delta_{\rm C}$ = 11.5, 22.1, 39.5, 104.1, 114.6, 122.2, 125.8, 127.8, 128.6, 129.3, 131.4, 136.7, 143.4, 168.6, 170.5. IR (neat) v_{max} 1676, 1736 (C=O), 3337, 3431 (NH₂) cm⁻¹. Anal. Calcd for C₁₅H₁₄N₂O₂: C, 7.85; H, 5.55; N, 11.02. Found: C, 70.46; H, 5.45; N, 10.91.

2-Bromomethyl-1-dibromometyl-3-nitrobenzene (4)



A mixture of 3-nitro-*o*-xylene (5.56 g, 36.8 mmol), NBS (33.0 g, 186 mmol), and BPO (4.03 g, 16.6 mmol) in CCl₄ (120 ml) was refluxed for 52 h. The produced succinimide was filtered off and the filtrate was washed with aqueous Na₂S₂O₃, dried (MgSO₄). The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (Hexane : AcOEt = 25 : 1) to afford tribromide **4** (11.59 g, 81 %). Pale yellow crystals, mp 69–70°C. ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ = 4.73 (s, 2H), 7.12 (s, 1H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.86 (dd, *J* = 1.2, 8.1 Hz, 1H), 8.28 (d, *J* = 8.1 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) $\delta_{\rm C}$ = 21.5, 34.5, 126.0, 126.7, 130.3, 135.1, 143.2, 149.4. IR (neat) $v_{\rm max}$ 1530, 1339 (N=O), 1264, 1177 (CH₂Br) cm⁻¹. Anal. Calcd for C₈H₆NO₂Br₃: C, 24.77; H, 1.56; N, 3.61. Found: C, 24.84; H, 1.48; N, 3.49.

N-Propyl-3,4-dihydro-5-nitronaphthalene-2,3-dicarboxyimide (5)



A mixture of tribromide **4** (1.00 g, 2.58 mmol), KI (1.65 g, 9.94 mmol), and *N*-propylmaleimide (0.55 g, 3.95 mmol) in DMF 15 ml was heated at 65°C for 18 h. The insoluble salts were filtered

off and the filtrate was concentrated under reduced pressure. The residue was treated with CHCl₃ and aqueous Na₂S₂O₃, and the organic layer was collected, dried (MgSO₄) and concentrated under reduced pressure. The residue was separated using a preparative liquid chromatography (silica gel, toluene : AcOEt = 15 : 1) to afford compound **5** (0.63 g, 85 %). Pale yellow cryatals, mp 130–132°C. ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ = 0.93 (t, *J* = 7.2 Hz, 3H), 1.66 (sext, *J* = 7.5 Hz, 2H), 2.88 (t, *J* = 16.2 Hz, 2H), 3.43 (ddd, *J* = 16.0, 7.1, 2.8 Hz, 1H), 3.61 (dt, *J* = 7.3, 3.9 Hz, 2H), 3.81 (dd, *J* = 16.9, 7.1 Hz, 1H), 7.41 (d, *J* = 2.7 Hz, 1H), 7.45 (t, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.3 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 11.5, 21.4, 24.5, 38.1, 40.6, 125.7, 127.9, 128.3, 130.0, 130.3, 133.6, 135.0, 150.1, 167.4, 174.5. IR (neat) v_{max} 1696 (C=O), 1517, 1332 (N=O) cm⁻¹. Anal. Calcd for C₁₅H₁₄N₂O₄: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.97; H, 4.67; N, 9.77.

N-propyl-5-nitronaphthalene-2,3-dicarboxyimide (6)



A mixture of compound **5** (0.10 g, 0.38 mmol) and DDQ (0.17 g, 0.76 mmol) in toluene (15 ml) was refluxed for 65 h. After cooled to r.t., 1,4-cyclohexadiene (0.05 g) was added to the mixture and the precipitate was filtered off. The filtrate was washed with aqueous Na₂CO₃, dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on silica gel (Toluene : AcOEt = 15 : 1) to afford compound **6** (50 mg, 46 %). Brown crystals, mp 184–185°C. ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ 0.99 (t, *J* = 7.5 Hz, 3H), 1.77 (sext, *J* = 7.5 Hz, 2H), 3.76 (t, *J* = 7.2 Hz, 2H), 7.80 (t, *J* = 7.8 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 8.42 (dd, *J* = 1.2, 7.8 Hz, 1H), 8.45 (s, 1H), 9.08 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) $\delta_{\rm C}$ = 11.5, 22.0, 40.4, 120.3, 124.9, 126.7, 127.6, 127.7, 129.4, 131.0, 136.4, 136.5, 148.4, 167.3, 167.3. IR (neat) $v_{\rm max}$ 1696 (C=O), 1510, 1406 (N=O) cm⁻¹. Anal. Calcd for C₁₅H₁₂N₂O₄: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.33; H, 4.32; N, 9.68.

N-propyl-5-aminonaphthalene-2,3-dicarboxyimide (5ANI)



A mixture of compound **6** (0.56 g, 1.97 mmol) and 10% Pd-C (0.03 g, 0.03 mmol) in DMF (20 ml) was vigorously stirred overnight under stream of H_2 . Pd-C was filtered off and the filtrate was concentrated under reduced pressure. The residue was chromatographed using a short

column of alumina (CH₂Cl₂) to afford **5ANI** (0.49 g, 98 %). Yellow crystals, mp 188–189°C. ¹H NMR (600 MHz, CDCl₃) $\delta_{\rm H}$ 0.98 (t, *J* = 7.2 Hz, 3H), 1.75 (sext, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 7.2 Hz, 2H), 4.39 (br, 2H), 6.94–6.96 (m, 1H), 7.46–7.48 (m, 2H), 8.24 (s, 1H), 8.35 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 11.5, 22.0, 40.0, 113.2, 118.0, 121.1, 124.7, 125.3, 126.5, 127.9, 130.1, 136.7, 144.8, 168.4, 168.5. IR (neat) $v_{\rm max}$ 1748, 1680 (C=O), 3439, 3364 (NH₂) cm⁻¹. HRMS. (ESI) *m/z* Calcd for C₁₅H₁₅N₂O₂ [M+H]⁺ 255.1135. Found. 255.1133.

1,2-Bis(dibromomethyl)-4-nitrobenzene (8)



A mixture of 4-nitro-*o*-xylene (1.50 g, 9.92 mmol), NBS (8.83 g, 49.6 mmol), and BPO (0.32 g, 0.99 mmol) in CCl₄ (120 ml) was refluxed for 48 h. The produced succinimide was filtered off and the filtrate was washed with aqueous Na₂S₂O₃, dried (MgSO₄). The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (hexane : AcOEt = 3 : 1) to afford tetrabromide **8** (4.11 g, 89 %). Pale yellow crystals, mp 114–118°C (lit. 125–127°C)^{S7 1}H NMR (300 MHz, CDCl₃) δ 7.08 (s, 1H), 7.13 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 8.21 (dd, *J* = 2.4 , 8.7 Hz, 1H), 8.55 (s, 1H).

N-Propyl-6-nitronaphthalene-2,3-dicarboxyimide (9)



A mixture of tetrabromide **8** (4.00 g, 8.57 mmol), KI (5.69 g, 34.3 mmol), and *N*-propylmaleimide (1.79 g, 12.9 mmol) in DMF 15 ml was heated at 65°C for 20 h. The insoluble salts were filtered off and the filtrate was concentrated under reduced pressure. The residue was treated with CHCl₃ and aqueous Na₂S₂O₃, and the organic layer was collected, dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on silica gel (CH₂Cl₂) to afford compound **9** (1.58 g, 65%). mp 234–235°C ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H} = 0.99$ (t, *J* = 7.4 Hz, 3H), 1.77 (sext, *J* = 7.5 Hz, 2H), 3.76 (t, *J* = 7.5 Hz, 2H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.44 (s, 1H), 8.45 (dd, *J* = 2.1, 9.0 Hz, 1H), 8.53 (s, 1H), 8.99 (d, *J* = 2.4 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) $\delta_{\rm C} = 11.5$, 21.9, 40.3, 122.5, 124.3, 126.1, 126.2, 129.9, 131.4, 132.0, 134.6, 138.2, 147.4, 167.2, 167.3. IR (neat) $v_{\rm max}$ 1695 (C=O), 1541, 1334 (N=O) cm⁻¹. Anal. Calcd for C₁₅H₁₂N₂O₄ : C, 63.38; H, 4.25; N, 9.85. Found: C, 63.30; H, 3.95; N, 9.87.

N-Propyl-6-aminonaphthalene-2,3-dicarboxyimide (6ANI)



A mixture of compound **9** (1.00 g, 3.52 mmol) and 10% Pd-C (371 mg, 0.35 mmol) in DMF (60 ml) was vigorously stirred overnight under stream of H₂. Pd-C was filtered off and the filtrate was concentrated under reduced pressure. The residue was chromatographed using a short column of alumina (CH₂Cl₂) to afford **6ANI** (0.85 g, 95 %). Brown crystals, mp 156–158°C. ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H} = 0.97$ (t, J = 7.5 Hz, 3H), 1.73 (sext, J = 7.5 Hz, 2H), 3.68 (t, J = 7.2 Hz, 2H), 4.17 (br, 2H), 7.08 (dd, J = 2.1, 8.4 Hz, 1H), 7.12 (d, J = 2.1 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 8.03 (s, 1H), 8.14 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) $\delta_{\rm C} = 11.5$, 22.0, 39.8, 110.5, 120.4, 122.2, 124.2, 124.7, 128.9, 129.1, 131.8, 137.7, 147.5, 168.7, 168.8. IR (neat) $v_{\rm max}$ 1755, 1685 (C=O), 3358, 3307 (NH₂) cm⁻¹. HRMS (FAB) *m/z* Calcd for C₁₅H₁₅N₂O₂ [M+H]⁺ 255.1135. Found 255.1138.



Figure S1 Absorption (blue) and fluorescence excitation (red) spectra of **1ANI** (a), **5ANI** (b), and **6ANI** (c). The asterisked peaks are the scatter of the monitoring light.



Figure S2 Experimentally obtained and peak-fitted absorption bands in the long-wavelength region of **6ANI** in various solvents. The red lines in the middle panels in each spectrum show the experimentally observed absorption spectra. The absorption bands are resolved by using the Gaussian function and the resolved bands are displayed in the lower panels in each spectrum. The absorption peak wavenumber values are shown in the resolved spectra. The dotted blue lines show the simulated spectra (sum of the resolved absorption bands) and the difference between the experimental and simulated spectra (Res. [%]) are shown in the upper panels of each spectrum. The peak fitting accuracy for the low-wavenumber region (< 30000 cm⁻¹) is within a few percent.



Figure S3 Fluorescence decay profiles (blue) of **1ANI** (a), **5ANI** (b), and **6ANI** (c) in various solvents, and the excitation lamp profiles (red). The decay profiles were analysed by single-exponential fitting and the τ_F values were shown with each decay curves. Ex. and Mon. indicate the wavelengths used for excitation of the sample and monitoring the fluorescence, respectively.



Figure S4 Fluorescence spectra of **1ANI** (...), **5ANI** (—) and **6ANI** (---) in a mixture of MeOH : $H_2O = 90:10 \text{ v/v}$. The asterisked band is second scatter of the excitation light.



Figure S5 Fluorescence and phosphorescence spectra of **1ANI** (a), **5ANI** (b) and **6ANI** (c) in EtOH glass at 77 K.



Figure S6 Absorption spectra of **ANIs** during photoirradiation in (a) MeCN at 300 nm and (b) MeOH at 350 nm: The solutions of **ANIs** were irradiated with a Xe-lamp of the fluorescence spectrophotometer under the conditions for fluorescence measurements and the absorption spectra were collected with 10-minutes of interval in 0–60 min time course (seven spectral lines overlap in each spectrum). The insets display absorbance during the irradiation at the wavelength shown in the axis labels.

Table S1 Optimized geometry of **1ANI** (B3LYP/6-31+G(d)).

E(RB3LYP) -840.07785443 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Υ	Z
	·				
1	6	0	4.844849	-1.01/586	0.240/10
2	6	0	3.631721	-1.667086	0.122860
3	6	0	2.412104	-0.947663	0.032471
4	6	0	2.459051	0.490691	0.058121
5	6	0	3.718099	1.124916	0.193166
6	6	0	4.887880	0.392144	0.281267
7	1	0	1.138516	-2.729036	-0.093377
8	1	0	5.765736	-1.590479	0.309097
9	1	0	3.592681	-2.753492	0.099857
10	6	0	1.164523	-1.643511	-0.075038
11	6	0	1.226487	1.248984	-0.048616
12	1	0	3.778700	2.208075	0.249004
13	1	0	5.840402	0.903897	0.388112
14	6	0	0.050514	0.520196	-0.144640
15	6	0	0.025866	-0.894474	-0.154389
16	6	0	-1.324205	1.011010	-0.290661
17	6	0	-1.400509	-1.315209	-0.292922
18	8	0	-1.720562	2.172543	-0.352276
19	8	0	-1.870170	-2.438738	-0.345851
20	6	0	-3.596458	-0.080181	-0.512775
21	1	0	-3.832815	0.821262	-1.086902
22	1	0	-3.886891	-0.956802	-1.100498
23	7	0	1.198817	2.618190	-0.006902
24	1	0	2.017460	3.144588	-0.272925
25	1	0	0.303389	3.051819	-0.212133
26	7	0	-2.145473	-0.125895	-0.366257
27	6	0	-4.336131	-0.068567	0.832325
28	6	0	-5.856452	-0.023314	0.643747
29	1	0	-4.054815	-0.964648	1.399656
30	-	0	-4.003764	0.801305	1.412940
31	1	0	-6.163997	0.876560	0.095949
32	1	0	-6.214814	-0.896242	0.083493
33	-	0	-6.371363	-0.015406	1.611101
	- 	~ 			

Table S2Optimized geometry of 5ANI (B3LYP/6-31+G(d)).

E(RB3LYP) -840.06935310 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	x	Y	7
		· , , , , , , , , , , , , , , , , , , ,			-
1	6	0	4.616710	-1.239156	0.296435
2	6	0	3.382635	-1.846893	0.178680
3	6	0	2.215552	-1.055494	0.037185
4	6	0	2.321468	0.384434	0.020399
5	6	0	3.624456	0.981818	0.113458
6	6	0	4.739676	0.162622	0.257827
7	1	0	0.845496	-2.752553	-0.073298
8	1	0	5.513020	-1.843721	0.407822
9	1	0	3.290084	-2.929247	0.194627
10	6	0	0.930653	-1.669007	-0.079953
11	6	0	1.136942	1.171516	-0.080249
12	1	0	5.725465	0.616189	0.336095
13	6	0	-0.073900	0.538212	-0.187593
14	6	0	-0.176774	-0.872798	-0.193424
15	6	0	-1.445346	1.102172	-0.307153
16	6	0	-1.618707	-1.227886	-0.320146
17	8	0	-1.798277	2.268556	-0.346613
18	8	0	-2.139705	-2.328225	-0.370074
19	6	0	-3.758830	0.103291	-0.506496
20	1	0	-3.963413	1.015290	-1.075980
21	1	0	-4.094754	-0.759243	-1.090557
22	7	0	-2.308582	-0.004913	-0.380491
23	1	0	1.169207	2.256153	-0.049371
24	7	0	3.762115	2.370069	0.123133
25	1	0	4.709540	2.704442	-0.004624
26	1	0	3.106160	2.897499	-0.438997
27	6	0	-4.477255	0.145314	0.849477
28	1	0	-4.228022	-0.763398	1.411712
29	1	0	-4.098432	0.998820	1.425733
30	6	0	-5.996592	0.258282	0.682707
31	1	0	-6.271533	1.172036	0.140705
32	1	0	-6.401434	-0.596840	0.126705
33	1	0	-6.496379	0.287262	1.657516

Table S3Optimized geometry of 6ANI (B3LYP/6-31+G(d)).

E(RB3LYP) -840.07214931 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	x	v	7
					_
1	6	0	-4.517758	1.014087	0.213061
2	6	0	-3.300860	1.648059	0.127762
3	6	0	-2.088589	0.915396	0.013899
4	6	0	-2.168453	-0.523938	-0.010972
5	6	0	-3.433469	-1.150446	0.073295
6	6	0	-4.603499	-0.408365	0.185234
7	1	0	-0.763994	2.650034	-0.057009
8	1	0	-5.430664	1.597747	0.309854
9	1	0	-3.256021	2.734395	0.148380
10	6	0	-0.825286	1.564655	-0.074833
11	6	0	-0.965106	-1.288173	-0.125404
12	6	0	0.228493	-0.622446	-0.207067
13	6	0	0.303608	0.792670	-0.182381
14	6	0	1.616674	-1.152778	-0.332145
15	6	0	1.733415	1.180486	-0.291180
16	8	0	1.994861	-2.310180	-0.393997
17	8	0	2.234557	2.291724	-0.314076
18	6	0	3.906151	-0.098441	-0.492378
19	1	0	4.136339	-0.989201	-1.085364
20	1	0	4.225960	0.787696	-1.049559
21	7	0	2.453471	-0.026997	-0.374258
22	1	0	-1.004016	-2.374274	-0.146283
23	1	0	-3.481573	-2.237538	0.055253
24	7	0	-5.845081	-1.019587	0.329231
25	1	0	-6.652611	-0.473971	0.055942
26	1	0	-5.910130	-1.985647	0.033908
27	6	0	4.616561	-0.161597	0.867061
28	1	0	4.253439	-1.038991	1.416972
29	1	0	4.342680	0.725431	1.452057
30	6	0	6.139218	-0.235499	0.708773
31	1	0	6.438648	-1.127815	0.144431
32	1	0	6.528139	0.643242	0.178771
33	1	0	6.633137	-0.279403	1.686071

			Coordinates (Anastrona)			
Center	ATOMIC	Atomic	Coordinates (Angstroms)			
Number	Number	Туре	Х	Y	Z	
1	6	0	-1.942553	-1.312320	-0.002289	
2	6	0	-2.273397	0.063193	-0.003958	
3	1	0	-0.377530	-2.804041	0.000864	
4	6	0	-0.616423	-1.744469	-0.001521	
5	6	0	-1.239843	1.028568	-0.005369	
6	6	0	0.066230	0.577731	-0.003796	
7	6	0	0.390927	-0.784264	-0.001755	
8	6	0	1.341456	1.364818	-0.000040	
9	6	0	1.868127	-0.920127	0.002157	
10	8	0	1.499321	2.571003	0.001478	
11	8	0	2.563095	-1.918746	0.005467	
12	7	0	2.354596	0.403112	0.002182	
13	1	0	-1.463507	2.092307	-0.012046	
14	7	0	-3.598928	0.463012	-0.058279	
15	1	0	-2.746100	-2.045289	-0.007225	
16	1	0	-4.300327	-0.206414	0.229982	
17	1	0	-3.809505	1.412301	0.220714	
18	1	0	3.340822	0.631430	0.004254	

Table S4Optimized geometry of 4-aminophthalimide **4API** (B3LYP/6-31+G(d)).E(RB3LYP) -568.47636680 a.u.



Figure S7 ¹H NMR spectrum of dimethyl 1-amino-2,3-naphthalenedicarboxylate **1** (300 MHz, CDCl₃).



Figure S8 (a) ¹H (600 MHz) and (b) ¹³C (150 MHz) NMR spectra of 1-amino-2,3-naphthalenedicarboxylic acid (acetone- d_6).



Figure S9 (a) ¹H (600 MHz) and (b) ¹³C (150 MHz) NMR spectra of 1-amino-2,3-naphthalenedcarboxylic anhydride **2** (acetone- d_6).



Figure S10 (a) ¹H (600 MHz) and (b) ¹³C (150 MHz) NMR spectra of *N*-propyl-1aminonaphthalene-2,3-dicarboxyimide **1ANI** (CDCl₃).



Figure S11 (a) 1 H (300 MHz) and (b) 13 C (150 MHz) NMR spectra of 2-bromomethyl-1-dibromometyl-3-nitrobenzene **3** (CDCl₃).





Figure S12 (a) ¹H (600 MHz) and (b) ¹³C (150 MHz) NMR spectra of *N*-propyl-3,4-dihydro-5-nitronaphthalene-2,3-dicarboxyimide **5** (CDCl₃).



Figure S13 (a) ¹H (300 MHz) and (b) ¹³C (150 MHz) NMR spectra of *N*-propyl-5nitronaphthalene-2,3-dicarboxyimide **6** (CDCl₃).



Figure S14 (a) ¹H (300 MHz) and (b) ¹³C (150 MHz) NMR spectra of *N*-propyl-5aminonaphthalene-2,3-dicarboxyimide **5ANI** (CDCl₃).



Figure S15 ¹H NMR spectrum of 1,2-bis(dibromomethyl)-4-nitrobenzene **8** (300 MHz, CDCl₃).



Figure S16 (a) ¹H- (300 MHz) and ¹³C (100 MHz) NMR spectra of *N*-propyl-6nitronaphthalene-2,3-dicarboxyimide **9** (CDCl₃).



Figure S17 (a) ¹H- (300 MHz) and ¹³C (100 MHz) NMR spectra of *N*-propyl-6-aminonaphthalene-2,3-dicarboxyimide **6ANI** (CDCl₃).

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