

## **Supporting Information (SI)**

### **New Core-Substituted Naphtalenediimides anchored on BiVO<sub>4</sub> for Visible Light-Driven Water Splitting**

**Simelys Hernández,<sup>a,b,\*</sup> Carminna Ottone,<sup>c</sup> Stefano Proto,<sup>d</sup> Kristhine Tolod,<sup>a</sup>  
Miriam Díaz de los Bernardos,<sup>d</sup> Albert Solé-Daura,<sup>e</sup> Jorge J. Carbó,<sup>e</sup> Cyril  
Godard,<sup>e</sup> Sergio Castellón,<sup>f</sup> Nunzio Russo,<sup>a</sup> Guido Saracco,<sup>b</sup> Carmen Claver,<sup>d,e\*</sup>**

<sup>a</sup> CREST group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy.

<sup>b</sup> Center for Sustainable Future Technologies (CSFT@Polito), Italian Institute of Technology, Corso Trento 21, 10129, Turin, Italy.

<sup>c</sup> School of Biochemical Engineering, Pontificia Universidad Catolica de Valparaiso. Av. Brasil 2085, Valparaiso, Chile.

<sup>d</sup> Centre Tecnològic de la Química a Catalunya (CTQC), CarrerMarcel·lí Domingo s/n, Edifici N5, 43007, Tarragona, Spain.

<sup>e</sup> Departament of Química Física i Inorgànica, Universitat Rovira i Virgili, CarrerMarcel·lí Domingo s/n, 43007, Tarragona, Spain.

<sup>f</sup> Department of Química Analítica i Química Orgànica, Universitat Rovira i Virgili, CarrerMarcel·lí Domingo s/n, 43007, Tarragona, Spain.

\*corresponding authors: E-mail: [simelys.hernandez@polito.it](mailto:simelys.hernandez@polito.it), [carmen.claver@ctqc.org](mailto:carmen.claver@ctqc.org)

## **Table of Contents:**

**Fig. S1:** NMR and FT-IR spectra of *N,N'*-dipyridyl 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (**dye 1**)

**Fig. S2:** NMR and FT-IR spectra of *N,N'*-Di-(2,6-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (**Br,Br-NDI**)

**Fig. S3:** NMR and FT-IR spectra of *N,N'*-Di-(2,6-diisopropylphenyl)-2-aminobenzoic acid-6-bromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (**dye 2**)

**Fig. S4:** NMR and FT-IR spectra of *N,N'*-Di-(2,6-diisopropylphenyl)-2-aminobenzoic acid-6-dimethylamine-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (**dye 3**)

**Fig. S5:** NMR and FT-IR spectra of *N,N'*-Di-(2,6-diisopropylphenyl)-2-aminobenzoic acid-6-bromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (**dye 4**)

**Fig. S6:** Photographs of dyes solutions in acetonitrile (a). UV-Visible spectra (b) and molecular structures (c) and of **dyes 1-4**.

**Fig. S7:** Characterization of **dye 1**-BiVO<sub>4</sub>.

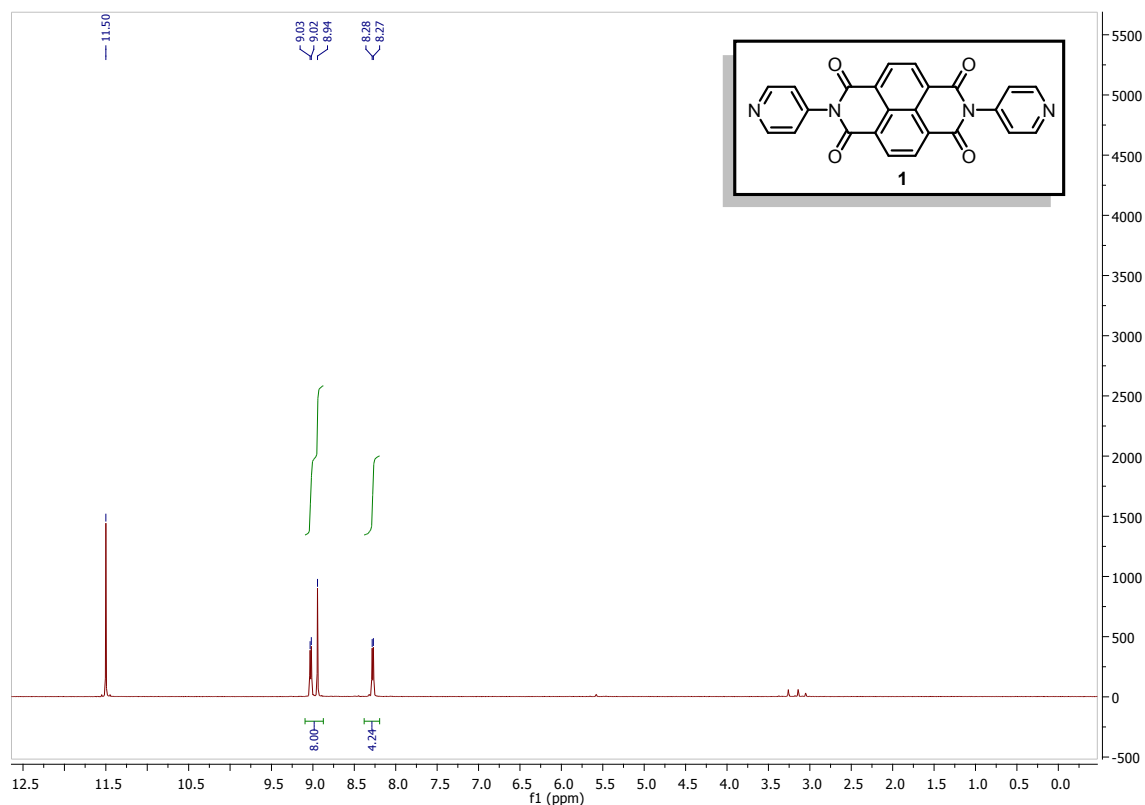
**Fig. S8:** TGA Analysis of dyes 2, 3 and 4 on BiVO<sub>4</sub>.

**Table S1:** Energy Levels of dyes.

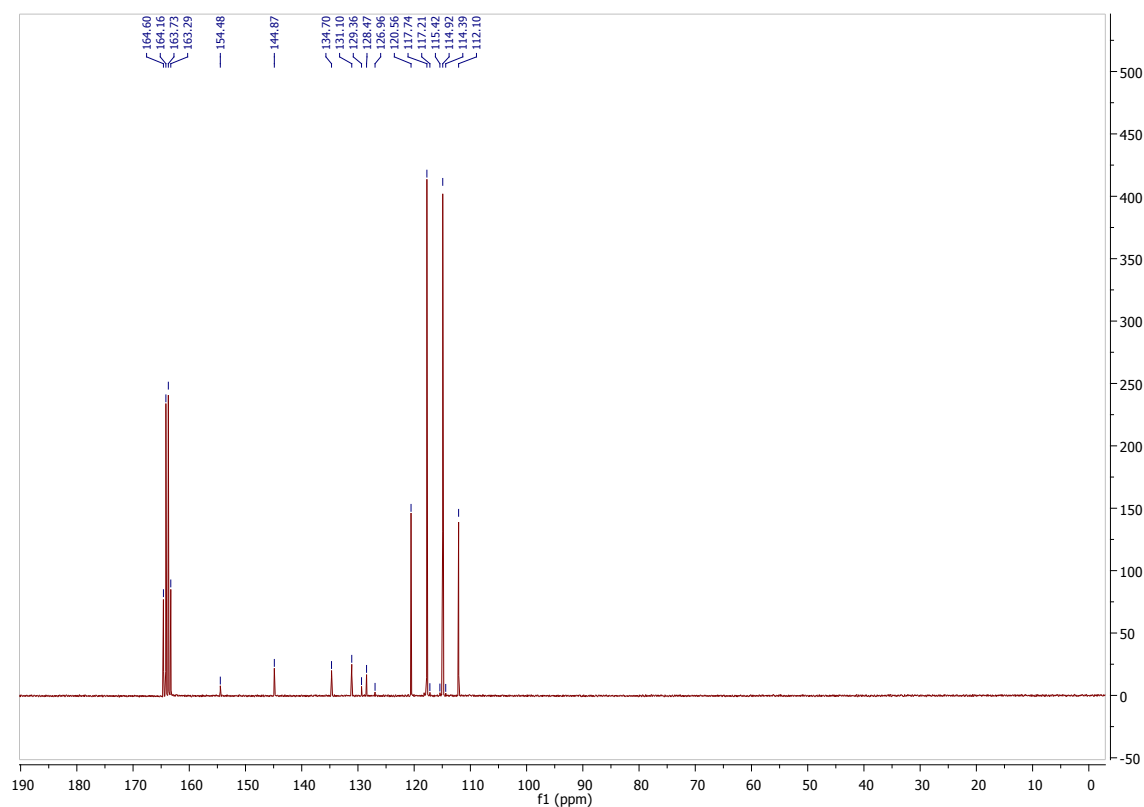
**Fig. S9:** Cyclic voltammetry curves for the dyes 1 to 4 for the experimental calculation of energy levels.

**Fig. S1: *N,N'*-dipyridyl 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (dye 1):**

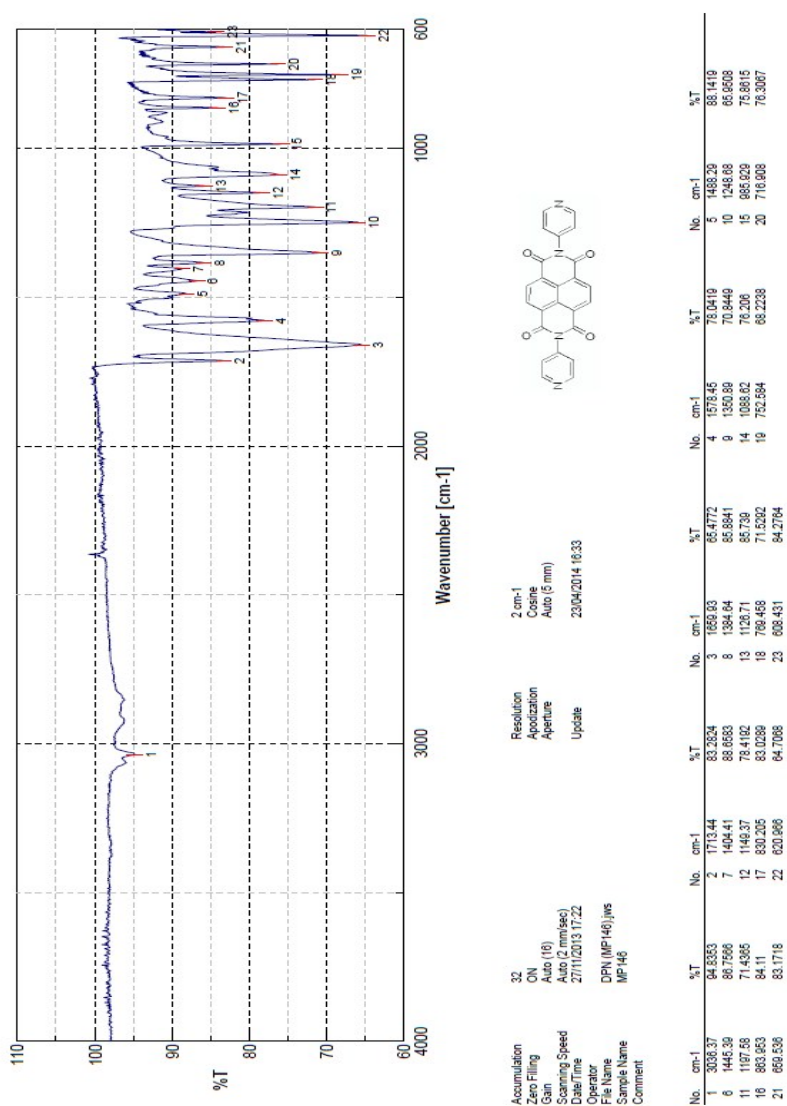
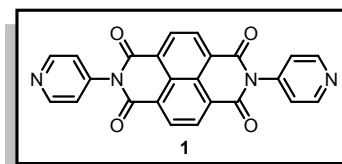
**(a)  $^1\text{H}$  NMR (400 MHz, TFA-d, 298K):**  $\delta$  9.03 (d,  $J$ = 4.0 Hz, 4H), 8.94 (s, 4H), 8.26 (d,  $J$ = 4.0 Hz, 4H).



**(b)  $^{13}\text{C}$  NMR (100.5 MHz, TFA-d, 298K):**  $\delta$  154.5, 145.5, 135.3, 131.7, 130.0, 129.1, 127.6.

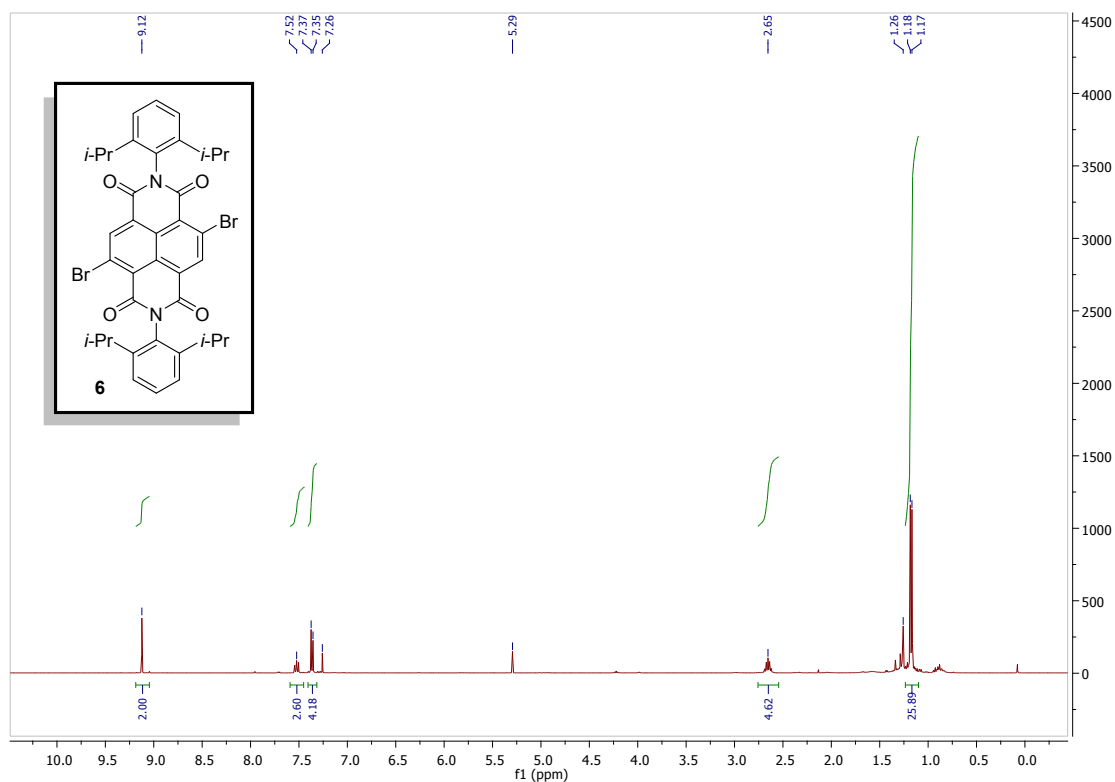


(c) **FT-IR:** 3036.37, 1710.44, 1659.93, 1578.45, 1488.29, 1445.39, 1384.64, 1350.89, 1248.68, 1197.58, 1149.37, 1126.71, 1088.62, 985.92, 863.95, 830.20, 769.46, 752.58, 716.91, 689.53, 620.96, 608.43  $\text{cm}^{-1}$ . High resolution Mass Spectroscopy analysis, **MS (HR-ESI)** yield  $m/z$ : observed 421.0942  $[M+H]^+$  and calculated 421.0937.

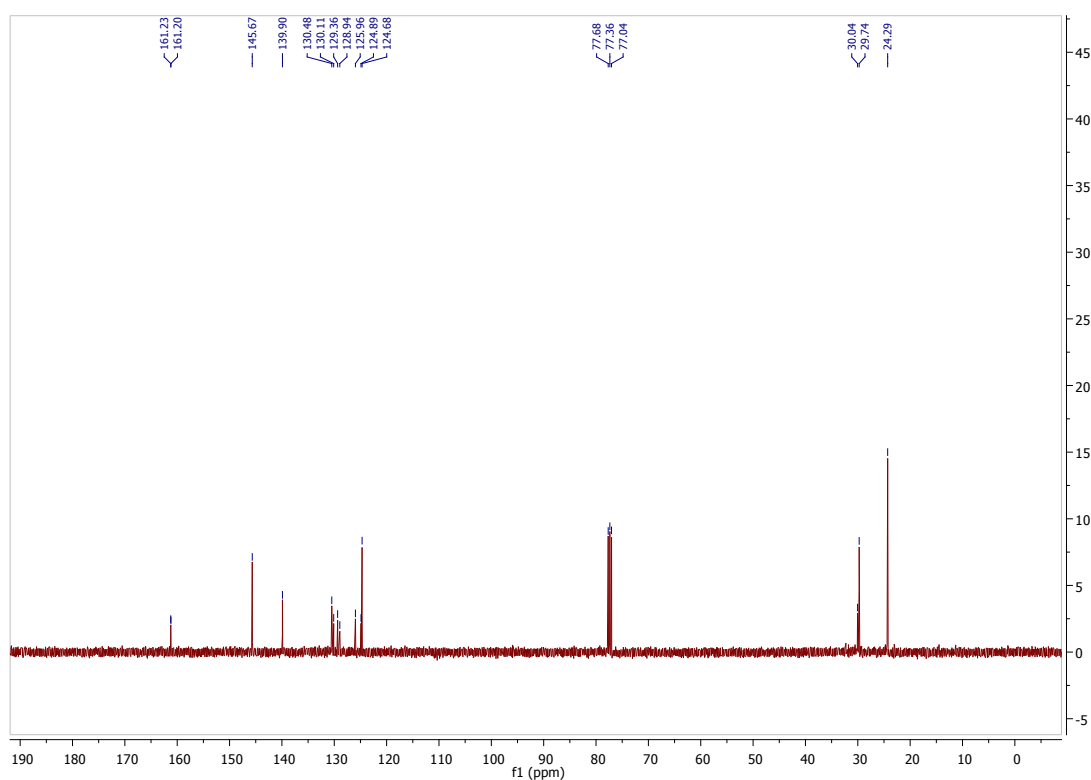


**Fig. S2: *N,N'*-Di-(2,6-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide(*Br,Br*-NDI):**

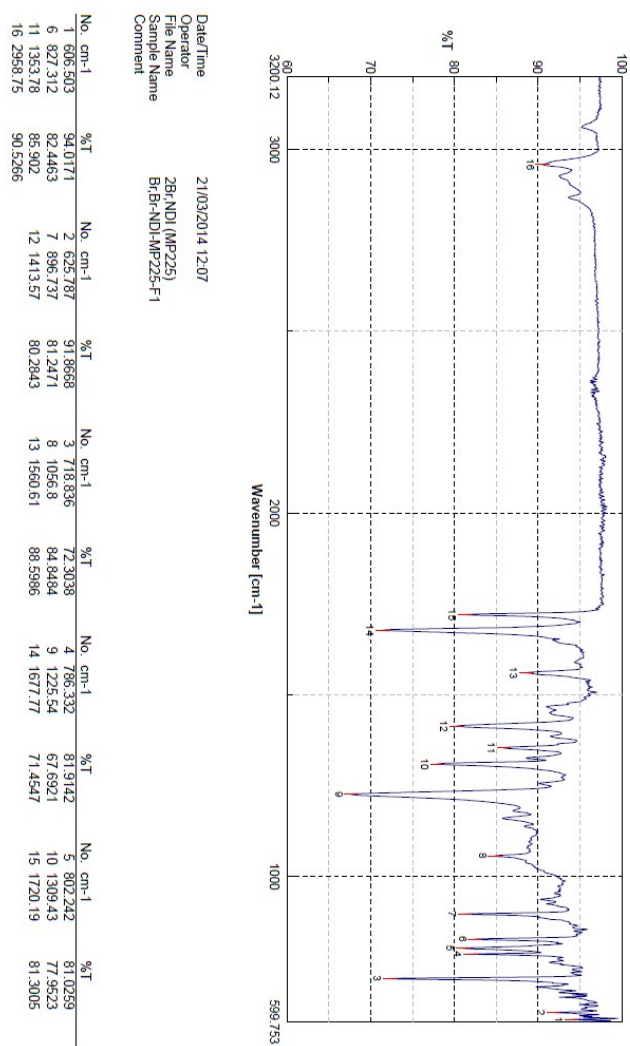
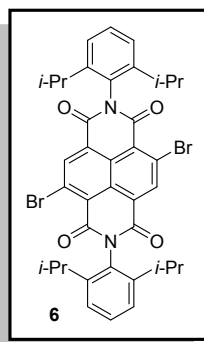
**(a)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):**  $\delta$  9.12 (s, 2H), 7.53 (d,  $J=8.0$  Hz, 2H), 7.34 (d,  $J=8.0$  Hz, 4H), 2.65 (sept,  $J=4.0$  Hz, 4H), 1.17 (d,  $J=4.0$  Hz, 24H).



**(b)  $^{13}\text{C}$  NMR (101.5 MHz,  $\text{CDCl}_3$ , 298K):**  $\delta$  161.2, 161.2, 145.6, 139.9, 130.5, 130.1, 129.4, 129.0, 125.6, 124.9, 124.7, 29.7, 24.3.



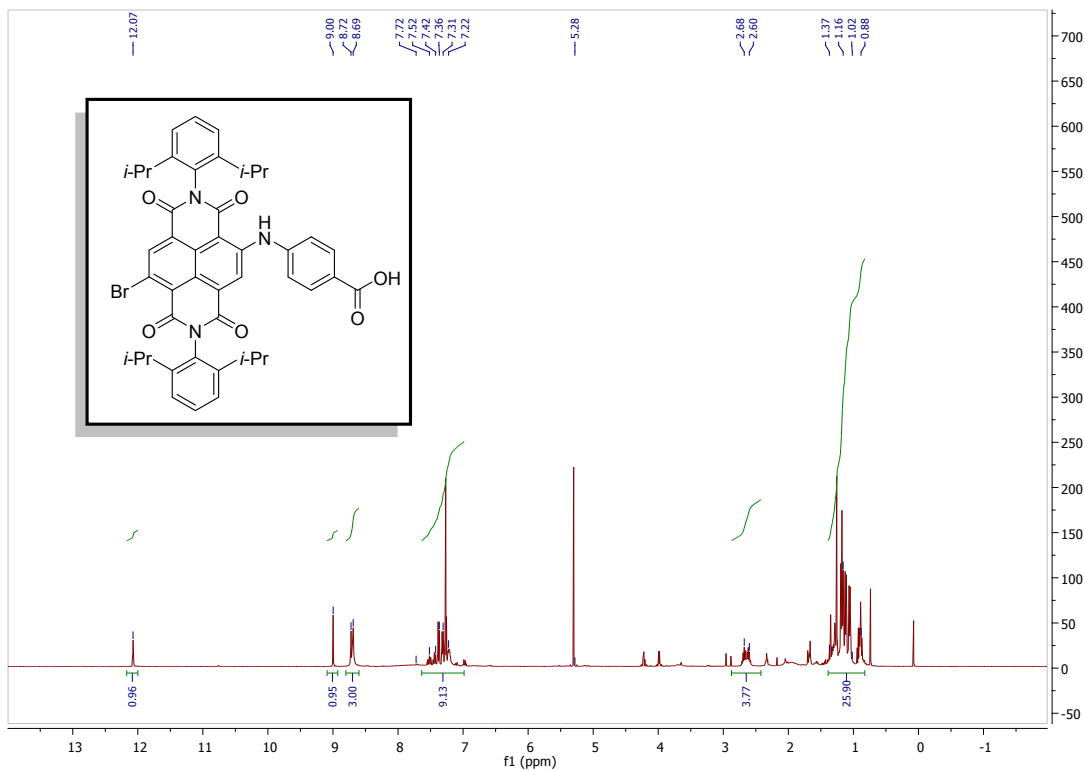
(c) **FT-IR:** 2958.75, 1720.19, 1677.77, 1560.61, 1413.57, 1353.78, 1309.43, 1225.55, 1056.80, 896.70, 827.70, 802.24, 786.33, 718.84, 625.79, 606.50  $\text{cm}^{-1}$ . **MS (HR-ESI)** yields  $m/z$ : observed 745.1063  $[\text{M}+\text{H}^+]$  and calculated 745.5240.



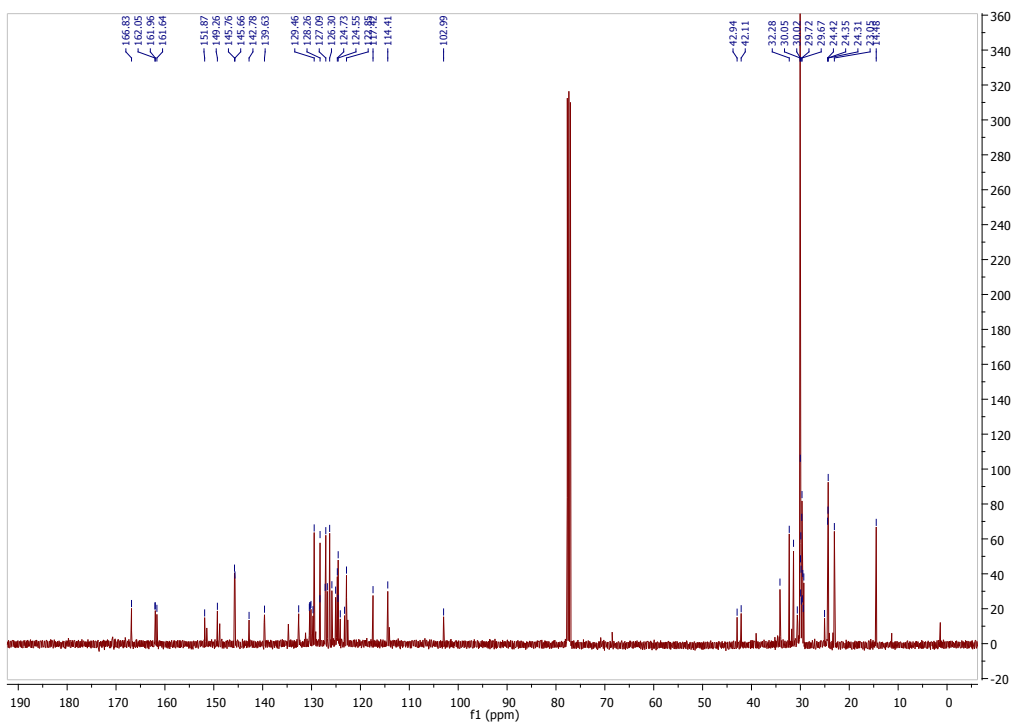
Date/Time 21/03/2014 12:07  
 Operator  
 File Name 2Br.NDI (MP25)  
 Sample Name Br-Br-NDI-MP25-F1  
 Comment

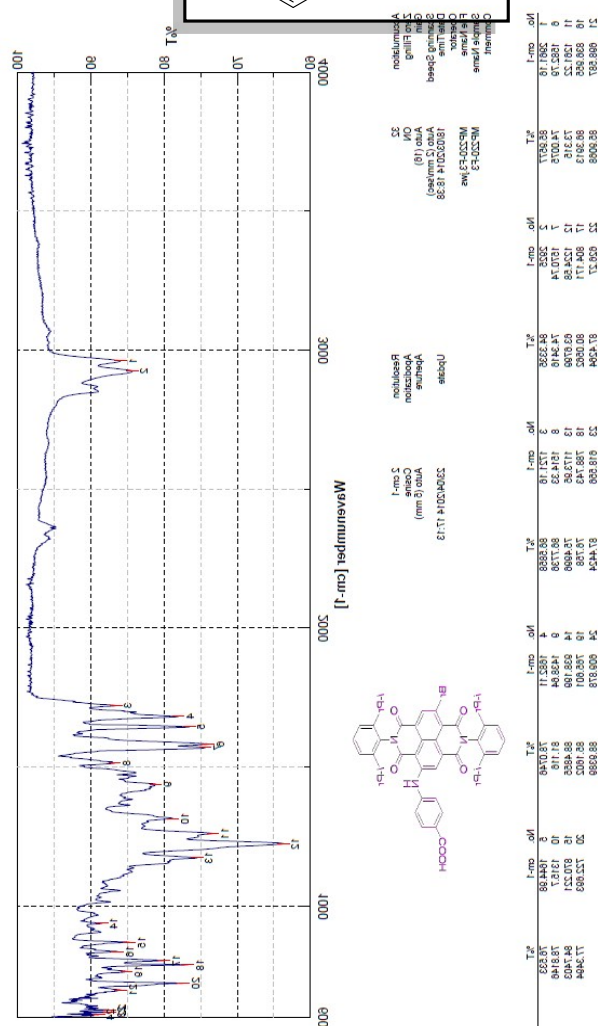
**Fig. S3: *N,N'*-Di-(2,6-diisopropylphenyl)-2-aminobenzoic acid-6-bromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (dye 2):**

**(a)  $^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  12.07 (s, 1H), 9.00 (s, 1H), 8.72 (s, 1H), 8.69 (d,  $J$  = 4.0 Hz, 2H), 7.51 (t,  $J$  = 8.0 Hz, 1H), 7.43 (t,  $J$  = 8.0 Hz, 1H), 7.37 (d,  $J$  = 8.0 Hz, 2H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 7.26 (d,  $J$  = 4.0 Hz, 2H), 2.67 (sept,  $J$  = 6.8 Hz, 2H), 2.61 (sept,  $J$  = 6.8 Hz, 2H), 1.37- 1.02 (m, 24H).



**b)  $^{13}\text{C}$  NMR** (101.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  166.8, 162.1, 161.6, 151.2, 149.2, 145.7, 142.8, 139.6, 132.6, 130.3, 129.4, 128.3, 127.2, 126.7, 126.3, 125.8, 124.7, 124.5, 124.1, 123.2, 122.8, 117.4, 102.9, 42.9, 42.1, 34.1, 32.3, 31.4, 24.3, 23.1, 14.45.

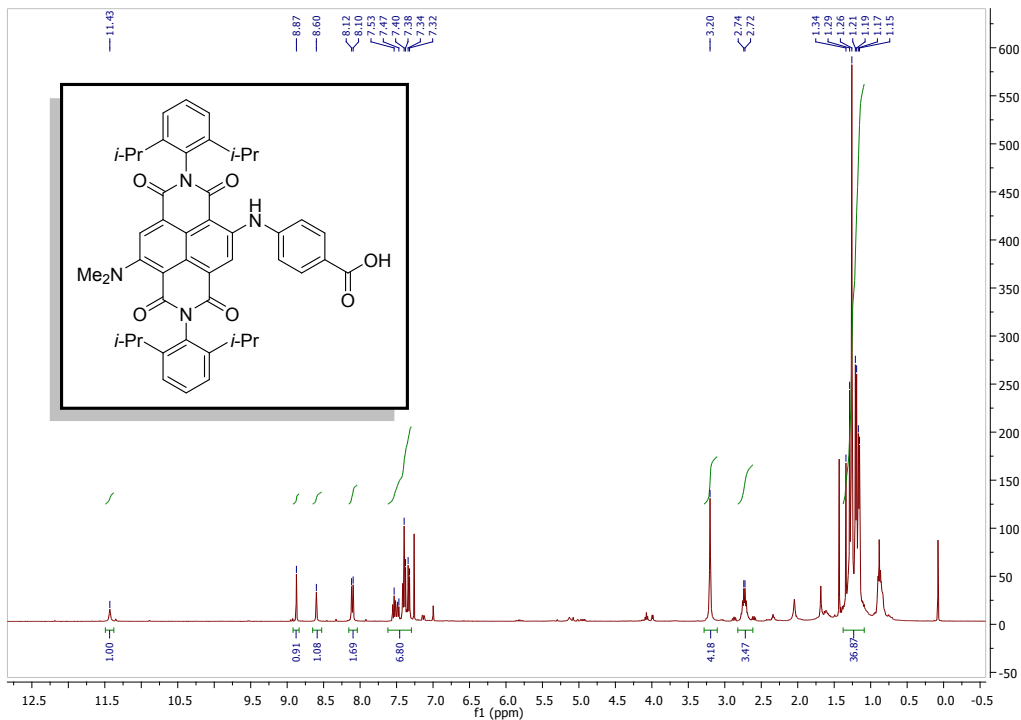


CC(C)c1ccc(cc1)N2C(=O)c3cc(Br)cc(NC(=O)c4ccc(cc4)C(=O)O)c3C(=O)N2C(=O)c5cc(C(C)C)cc(C(C)C)c5

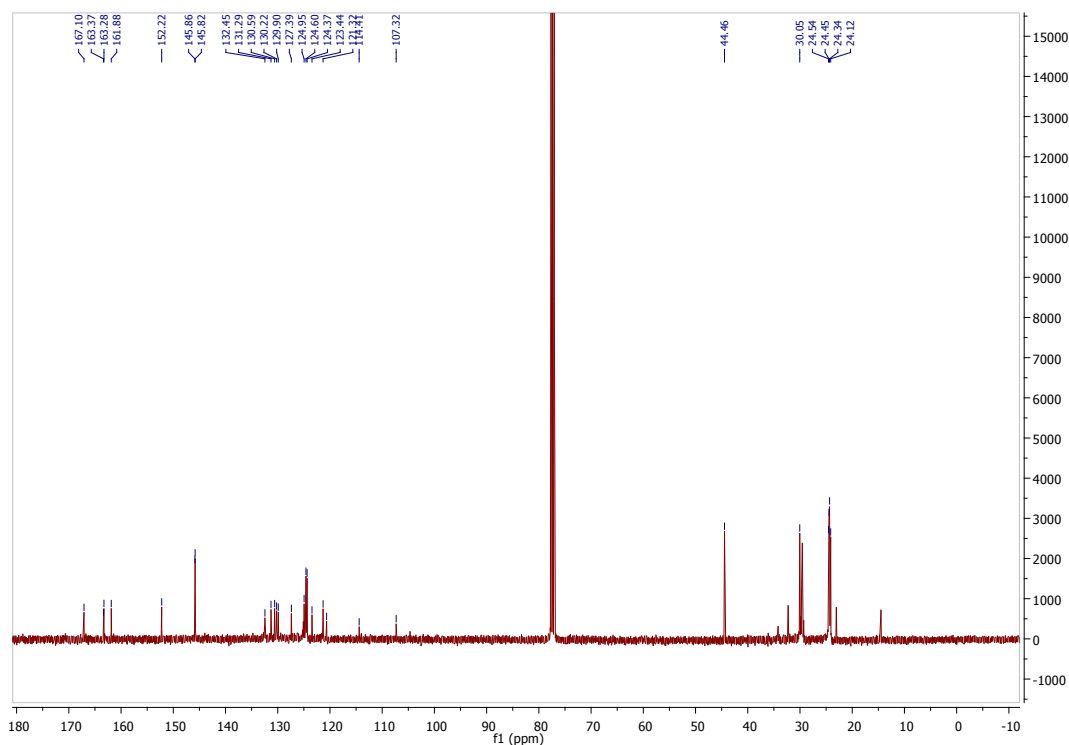


**Fig. S4: *N, N'*-Di-(2,6-diisopropylphenyl)-2-aminobenzoic acid-6-dimethylamine-naphthalene-1,4,5,8-tetracarboxylic acid bisimide (dye 3):**

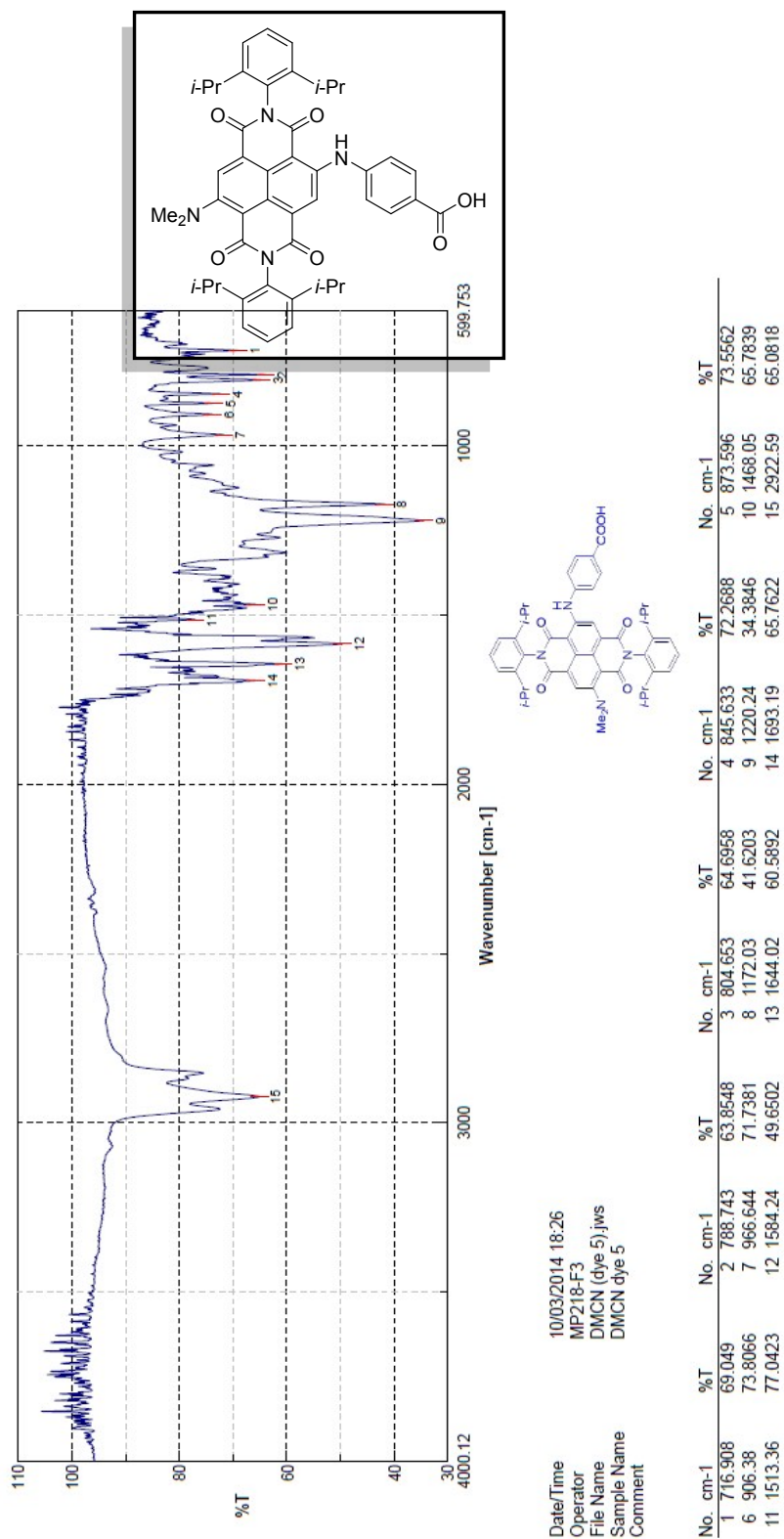
- (a)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  11.48 (s, 1H), 8.87 (s, 2H), 8.60 (s, 1H), 8.12 (d,  $J = 8.0$  Hz, 2H), 7.53 (t,  $J = 8.0$  Hz, 1H), 7.47 (t,  $J = 8.0$  Hz, 1H), 7.40-7.32 (m, 8H), 3.20 (s, 6H), 2.74 (m, 4H), 1.34- 1.15 (m, 24H).



- (b)  $^{13}\text{C}$  NMR (101.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.1, 163.4, 163.3, 161.9, 152.2, 145.8, 132.5, 131.3, 130.6, 130.2, 129.9, 127.4, 124.7, 124.6, 123.4, 121.3, 120.6, 114.2, 107.3, 44.5, 30.1, 24.5, 24.4, 24.3, 24.1.

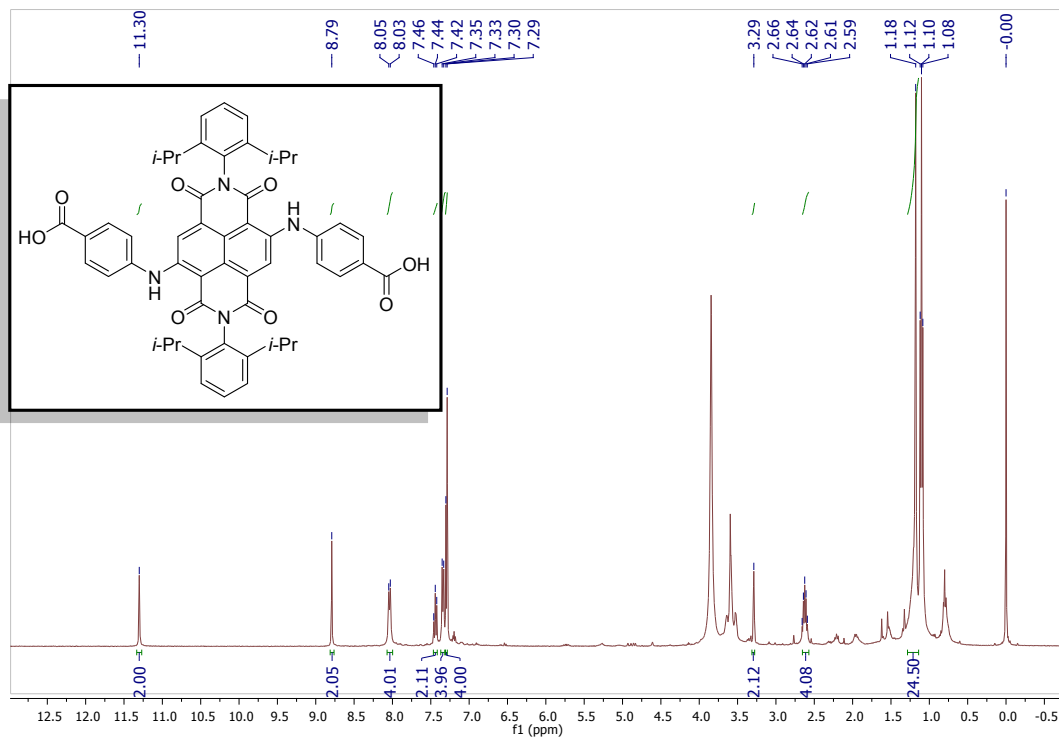


(c) **FT-IR:** 2922.59, 1693.19, 1644.02, 1584.24, 1513.36, 1468.05, 1220.24, 1173.03, 966.64, 906.38, 873.59, 845.63, 804.65, 788.74, 716.91  $\text{cm}^{-1}$ . **MS (HR-ESI)** yields  $m/z$ : observed 763.3509  $[\text{M}+\text{H}]^+$  and calculated 764.3574.

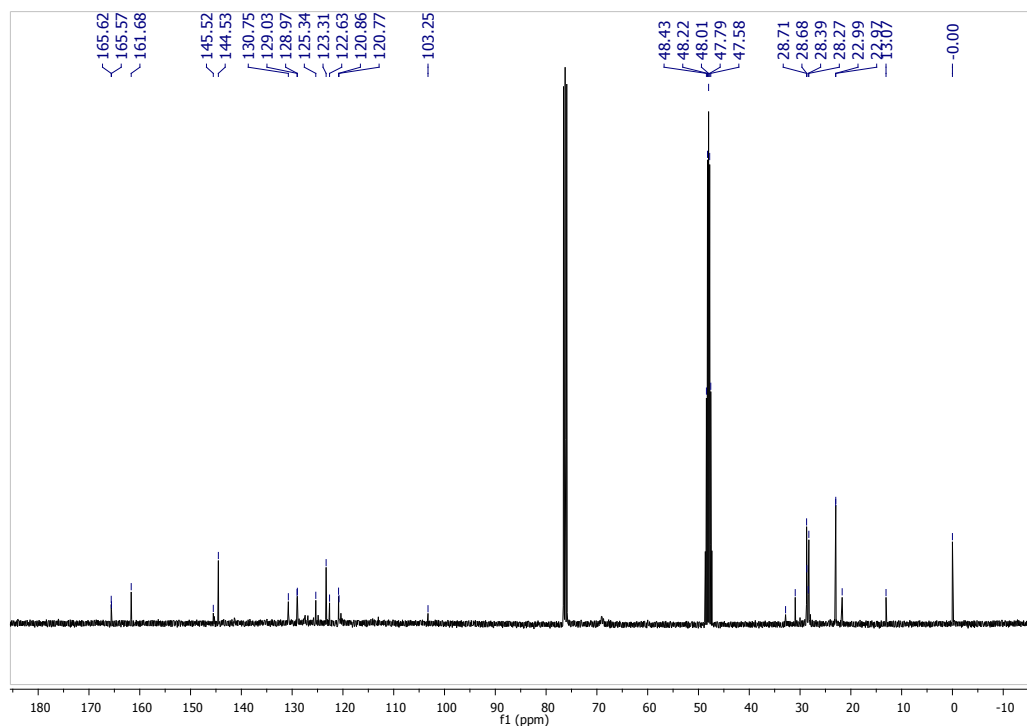


**Fig.S5: *N,N'*-Di-(2,6-diisopropylphenyl)-2-aminobenzoic acid-6-bromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (dye 4):**

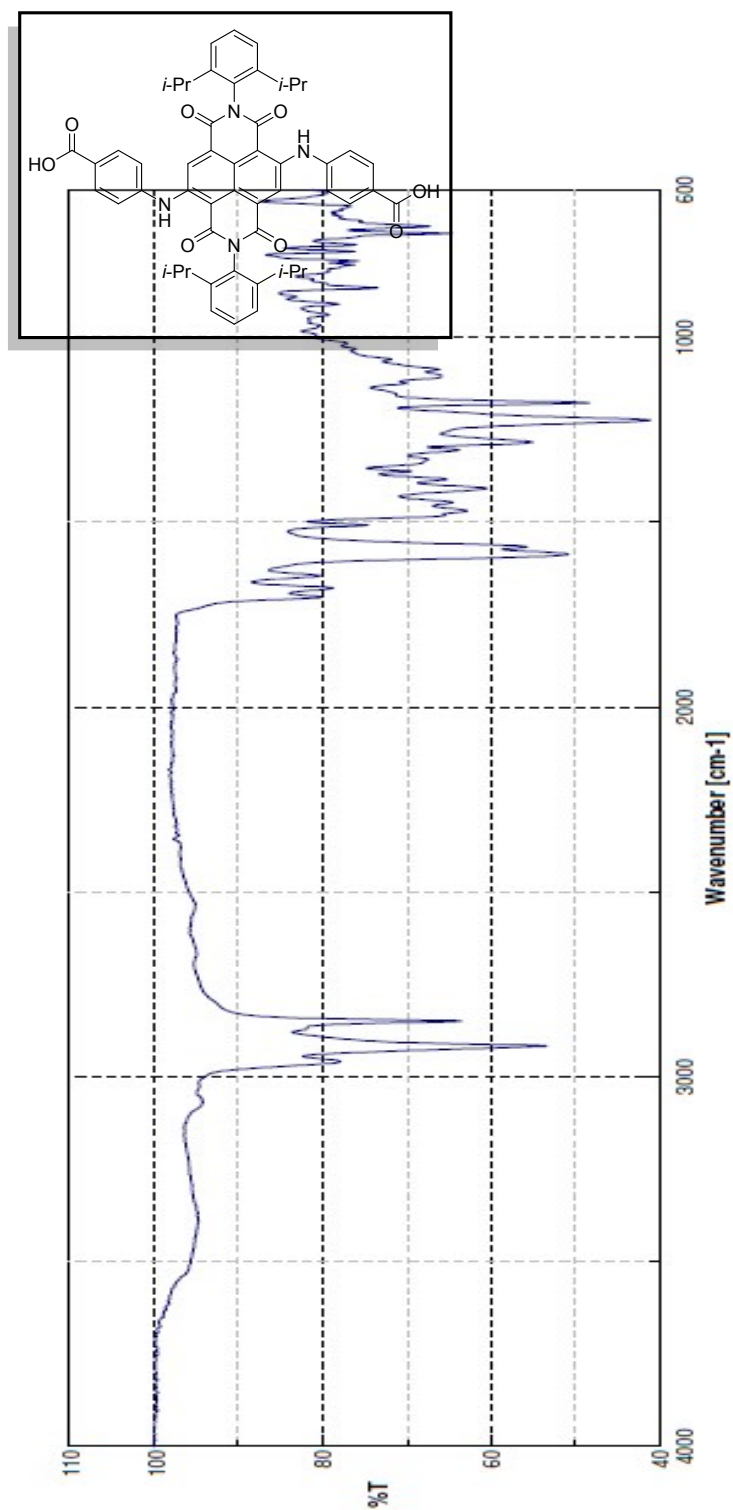
- (a)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ -MeOH, 298K):  $\delta$  11.30 (s, 2H), 8.79 (s, 2H), 8.04 (d,  $J = 8.0$  Hz, 4H), 7.44 (t,  $J = 8.0$  Hz, 2H), 7.34 (d,  $J = 8.0$  Hz, 4H), 7.29 (d,  $J = 8.0$  Hz, 4H), 3.29 (s, 2H), 2.66-2.59 (m, 4H), 1.18-1.08 (m, 24H).



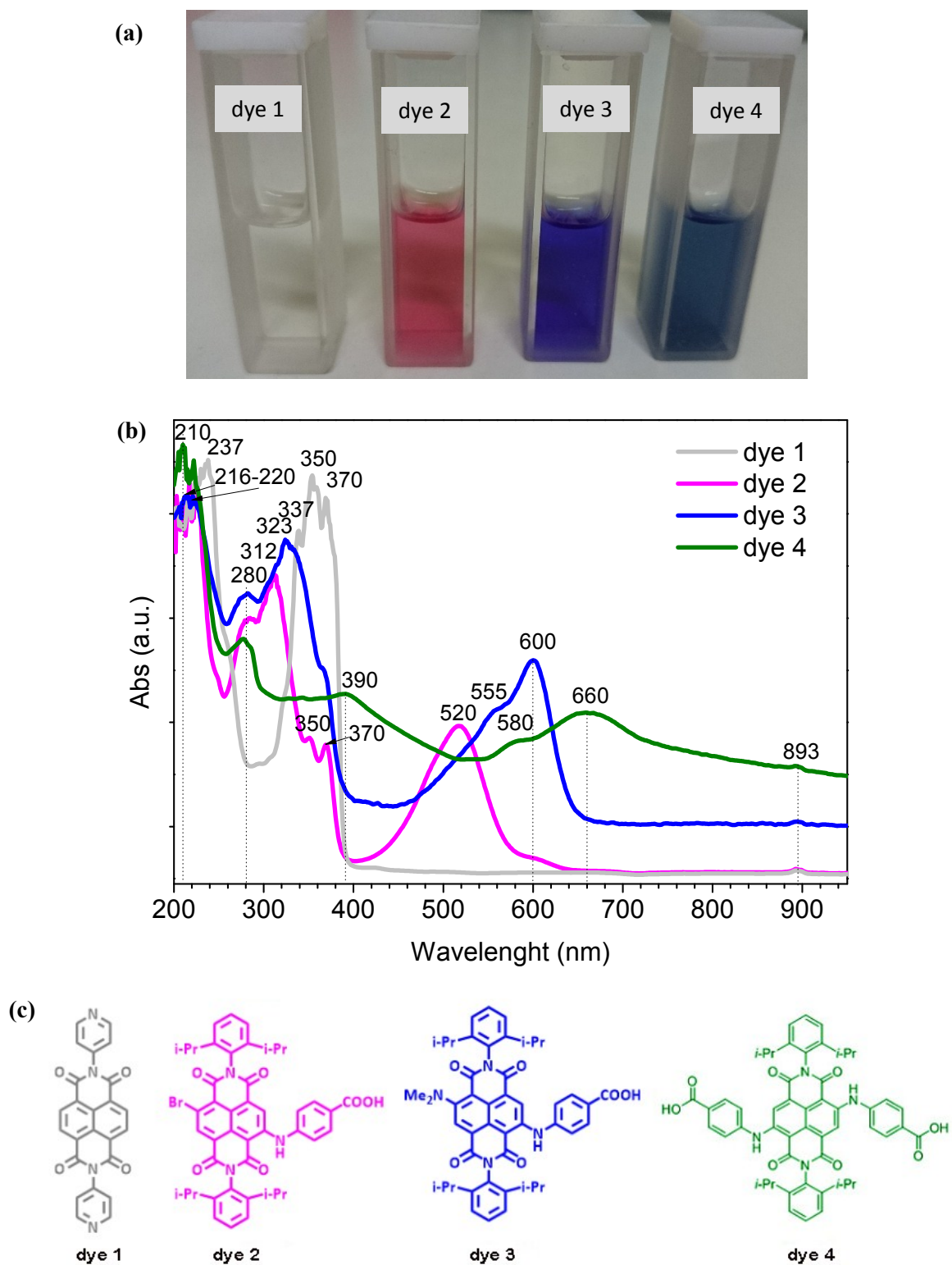
- (b)  $^{13}\text{C}$  NMR (101.5 MHz,  $\text{CD}_2\text{Cl}_2$ -MeOH):  $\delta$  165.6, 165.6, 161.7, 145.5, 144.5, 130.7, 129.0, 128.9, 125.3, 123.3, 122.6, 120.9, 120.7, 103.2, 32.8, 30.9, 28.7, 28.6, 28.4, 28.3, 23.0, 22.9, 21.7.



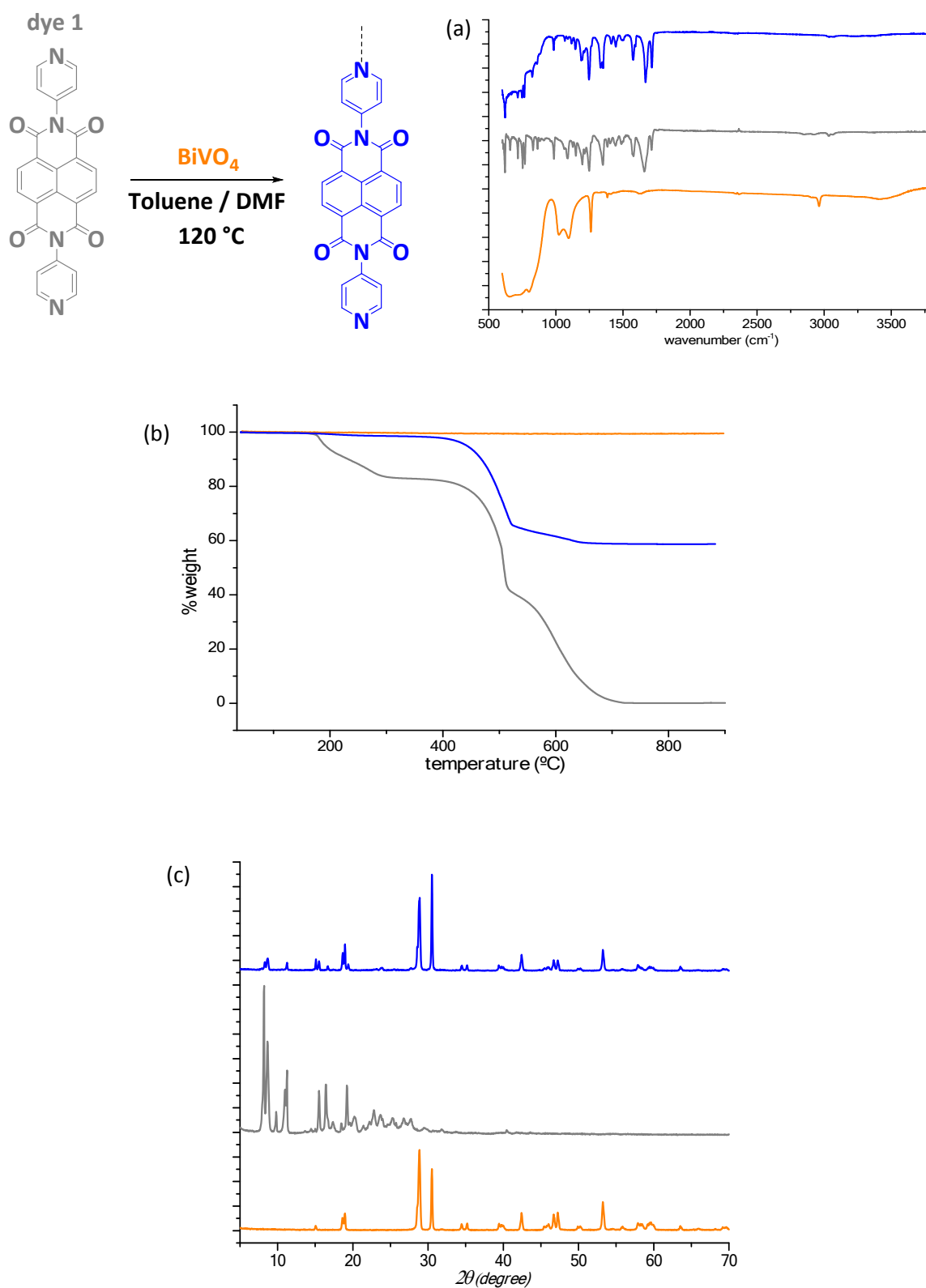
(c) **FT-IR:** 2927.08, 2861.70, 1682.01, 1648.86, 1600.05, 1477.57, 1411.26, 1280.49, 1231.69, 1190.24, 1100.00, 878.98, 797.02, 731.63, 699.40  $\text{cm}^{-1}$ . **MS (HR-ESI)** yieldsm/z: observed 857.3550  $[\text{M}+\text{H}]^+$  and calculated 858.35.



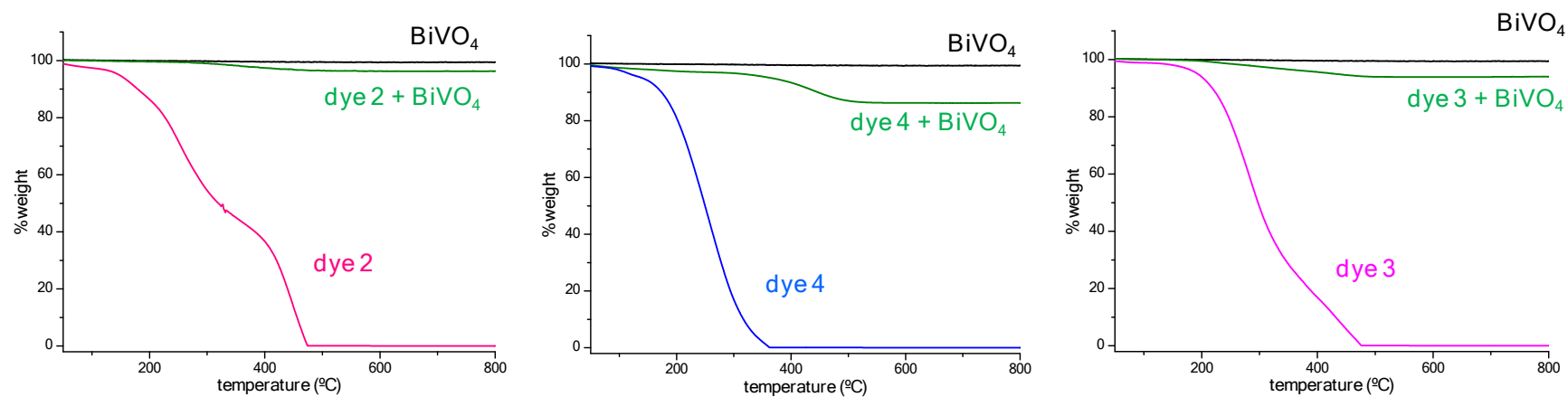
**Fig. S6: Photographs of dyes solutions in acetonitrile (a).UV-Visible spectra (b) and molecular structures (c) and of dyes 1-4.**



**Fig. S7: Characterization of dye 1-BiVO<sub>4</sub>:** (a) FTIR spectrum and (b) TGA under air atmosphere and (c) XRD spectrum. Legend: bare Dye 1 (gray), bare BiVO<sub>4</sub> (orange) and dye1 substituted BiVO<sub>4</sub> (blue).



**Fig. S8: TGA Analysis of dyes 2, 3 and 4 on  $\text{BiVO}_4$ .** Legend: dye 2 (red), dye 3 (pink), dye 4 (blue), bare  $\text{BiVO}_4$  (black) and dye-substituted  $\text{BiVO}_4$  (green).



**Table S1: Energy Levels of dyes.** Comparison of computed (BP86 and PBE functionals) and experimentally determined (Exp.) HOMO and LUMO energies, and band gap ( $E_g$ ). Energies, mean values between experimental and BP86 results, and average errors respect to experimental values (av. error) in eV.

|                  | HOMO [eV] |       |            |       | LUMO [eV] |       |            |       | E <sub>g</sub> [eV] |      |            |
|------------------|-----------|-------|------------|-------|-----------|-------|------------|-------|---------------------|------|------------|
|                  | Exp.      | BP86  | Mean value | PBE   | Exp.      | BP86  | Mean value | PBE   | Exp.                | BP86 | Mean value |
| <b>Dye 1</b>     | -6.35     | -6.20 | -6.28      | -6.04 | -3.66     | -4.13 | -3.9       | -4.04 | 2.69                | 2.07 | 2.38       |
| <b>Dye 2</b>     | -5.53     | -5.49 | -5.51      | -5.39 | -3.95     | -4.01 | -3.98      | -3.90 | 1.58                | 1.48 | 1.53       |
| <b>Dye 3</b>     | -5.16     | -4.94 | -5.05      | -4.84 | -3.65     | -3.69 | -3.67      | -3.58 | 1.51                | 1.26 | 1.39       |
| <b>Dye 4</b>     | -5.4      | -5.09 | -5.25      | -4.98 | -3.82     | -3.88 | -3.85      | -3.78 | 1.57                | 1.21 | 1.40       |
| <b>av. error</b> |           | 0.18  |            | 0.30  |           | 0.16  |            | 0.13  |                     | 0.34 | 0.17       |

**Fig. S9:** Cyclic voltammetry curves for the **dyes 1 to 4** for the experimental calculation of energy levels. Experimental conditions: acetonitrile electrolyte, scan rate of 100 mV/s under N<sub>2</sub> flow. The values of onset-potential of oxidation ( $E_{ox}$ ) and reduction ( $E_{red}$ ) are given in the legend.

