

Supporting Information:

Novel Naphthalimide-amine Based Photoinitiators Operating under Violet and Blue LEDs and Usable for Various Polymerization Reactions and Synthesis of Hydrogels.

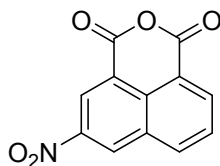
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Syntheses of DNNDs

General

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy and NMR were recorded by the Spectropole of Aix-Marseille University. The HRMS mass spectral analysis were performed with a SYNAPT G2 HDMS (Waters) mass spectrometer. ¹H and ¹³C NMR were determined at room temperature in 5 mm o.d. tubes on a Bruker AC 400 spectrometer of the Spectropole: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peak DMSO-d₆ (2.50 ppm), CDCl₃ (7.26 ppm) and the ¹³C chemical shifts, determinate by ¹³C-APT experiment, were referenced to the solvent peak DMSO-d₆ (39.5 ppm), CDCl₃ (77 ppm). Chromatography on atmospheric pressure column was performed on silica gel 60 with particle size of 40-63 nm (Merck). Eluents were specified for each operation. All these dyes were prepared with analytical purity up to accepted standards for new organic compounds (>98%), which were checked by high field NMR analysis.

3-nitro-1,8-naphthalic acid anhydride

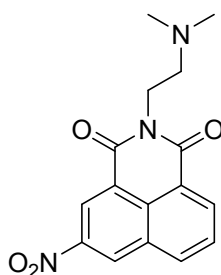


C₁₂H₅NO₅
MW = 243.17 g.mol⁻¹
Exact Mass: 243.0168

¹ Formerly, ENSCMu-UHA, 3 rue Alfred Werner, 68093 Mulhouse Cedex, Fr

A solution of HNO₃ (1.6 mL, 25.2 mmol, 1 eq.) in concentrated H₂SO₄ (5 mL) was added dropwise to the mixture of 1,8-naphthalic acid anhydride (5 g, 25.2 mmol) and concentrated H₂SO₄ (20 mL) at 0 °C. The reaction was allowed to stir at room temperature for 17 hours and poured into ice water. The resulting precipitate was filtered, washed with water, and recrystallized with glacial acetic acid to afford a compound as pale yellow solid, m.p. 247 °C (3.41g, 14.02 mmol, 56 % yield). ¹H NMR (DMSO d₆) δ(ppm): 8.10 (t, 1H, J = 7.8 Hz), 8.72 (d, 1H, J = 7 Hz), 8.85 (d, 1H, J = 8.3 Hz), 8.94 (d, 1H, J = 1.8 Hz), 9.55 (d, 1H, J = 1.8 Hz); ¹³C NMR (DMSO d₆) δ(ppm): 119.9 (C_q), 121.4 (C_q), 124.2 (CH_{Ar}), 129.5 (CH_{Ar}), 130.6 (CH_{Ar}), 130.9 (C_q), 131.7 (C_q), 135.4 (CH_{Ar}), 137.2 (CH_{Ar}), 145.9 (C_q), 159.6 (C=O), 159.9 (C=O); HRMS (ESI MS) m/z: theor: 244.0240 found: 244.0239 ((M+H)⁺ detected).

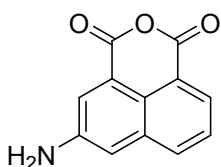
N-((dimethylamino)ethyl)-3-(nitro)-1,8-naphthalimide (DNND1)



C₁₆H₁₅N₃O₄
 MW = 313.31 g.mol⁻¹
 Exact Mass: 313.1063

A mixture of 3-nitro-1,8-naphthalic anhydride (1.0 g, 4.11 mmol) and N,N-dimethylethylenediamine (0.47 mL, 4.32 mmol, 1.05 eq.) in ethanol (50 mL) was refluxed for 2.5 hours. Obtained solution was cooled with an ice/water bath. Then resulting precipitate was filtered, washed several times with ethanol and pentane to afford a compound as a brown solid, m.p. 141 °C (910 mg, 2.9 mmol, 71 % yield). ¹H NMR (CDCl₃) δ(ppm): 2.34 (s, 6H), 2.67 (t, 2H, J = 6.7 Hz), 4.35 (t, 2H, J = 6.7 Hz), 7.94 (t, 1H, J = 7.8 Hz), 8.42 (d, 1H, J = 8.3 Hz), 8.78 (d, 1H, J = 7.3 Hz), 9.13 (s, 1H), 9.30 (s, 1H); ¹³C NMR (CDCl₃) δ(ppm): 38.6 (CH₂), 45.8 (CH₃), 56.9 (CH₂), 123.2 (C_q), 124.2 (CH_{Ar}), 124.7 (C_q), 128.9 (CH_{Ar}), 129.0 (CH_{Ar}), 130.2 (C_q), 131.0 (C_q), 134.4 (CH_{Ar}), 135.5 (CH_{Ar}), 146.3 (C_q), 162.5 (C=O), 163.1 (C=O); HRMS (ESI MS) m/z: theor: 314.1135 found: 314.1136 ((M+H)⁺ detected).

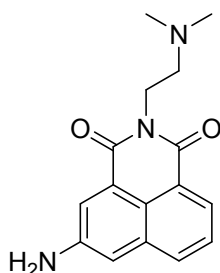
3-amino-1,8-naphthalic acid anhydride



C₁₂H₇NO₃
 MW = 213.19 g.mol⁻¹
 Exact Mass: 213.0426

A mixture of 3-nitro-1,8-naphthalic anhydride (1.0 g, 4.11 mmol) and tin (II) chloride (7.0 g, 31.02 mmol, 7.5 eq.) in concentrated HCl (7 mL) was refluxed for 2 hours. The resulting precipitate was filtered, washed several times with concentrated HCl and dried under vacuum to afford a compound as a yellow solid, m.p. 310 °C (1.13 g, 5.3 mmol, 94 % yield). ¹H NMR (DMSO d₆) δ(ppm): 7.37 (d, 1H, J = 2 Hz), 7.65 (t, 1H, J = 7.8 Hz), 7.96 (t, 1H, J = 7.8 Hz), 8.09 (d, 1H, J = 7.3 Hz), 8.13 (d, 1H, J = 8 Hz); ¹³C NMR (DMSO d₆) δ(ppm): 112.6 (CH_{Ar}), 118.5 (C_q), 119.3 (C_q), 122.9 (C_q), 123.1 (CH_{Ar}), 127.1 (CH_{Ar}), 127.3 (CH_{Ar}), 132.6 (CH_{Ar}), 133.6 (C_q), 148.2 (C_q), 160.9 (C=O), 161.0 (C=O); HRMS (ESI MS) m/z: theor: 214.0499 found: 214.0499 ((M+H)⁺ detected).

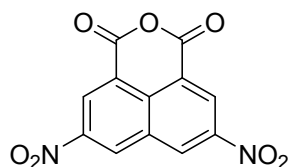
N-((dimethylamino)ethyl)-3-(amino)-1,8-naphthalimide (DNND3)



C₁₆H₁₇N₃O₂
 MW = 283.33 g.mol⁻¹
 Exact Mass: 283.1321

A mixture of 3-amino-1,8-naphthalic anhydride (700 mg, 3.28 mmol) and N,N-dimethylethylenediamine (0.38 mL, 3.45 mmol, 1.05 eq.) in ethanol (20 mL) was refluxed for 2.5 hours. Obtained solution was cooled with an ice/water bath. Then resulting precipitate was filtered, washed several times with ethanol and pentane to afford a compound as a yellow solid, m.p. 162 °C (804 mg, 2.84 mmol, 86 % yield). ¹H NMR (DMSO d₆) δ(ppm): 2.19 (s, 6H), 2.48 (t, 2H, J = 7 Hz), 4.12 (t, 2H, J = 6.5 Hz), 6.0 (s, 2H), 7.28 (s, 1H), 7.61 (t, 1H, J = 7.7 Hz), 7.95 (s, 1H), 8.03 (d, 1H, J = 8.3 Hz), 8.07 (d, 1H, J = 7 Hz); ¹³C NMR (DMSO d₆) δ(ppm): 37.5 (CH₂), 45.4 (CH₃), 56.5 (CH₂), 111.7 (CH_{Ar}), 120.6 (C_q), 121.70 (C_q), 121.73 (CH_{Ar}), 122.5 (C_q), 125.4 (CH_{Ar}), 126.9 (CH_{Ar}), 131.5 (CH_{Ar}), 133.5 (C_q), 147.9 (C_q), 163.5 (C=O), 163.7 (C=O); HRMS (ESI MS) m/z: theor: 284.1394 found: 284.1396 ((M+H)⁺ detected).

3,6-dinitro-1,8-naphthalic acid anhydride

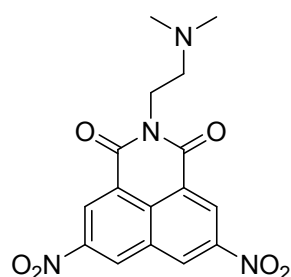


C₁₂H₄N₂O₇
 MW = 288.17 g.mol⁻¹
 Exact Mass: 288.0019

A solution of concentrated H₂SO₄ (20 mL) and 1,8-naphthalic acid anhydride (5 g, 25.2 mmol) was introduced in 100 mL two-neck flask then the mixture was cooled at 5 °C in ice

bath. A solution of HNO₃ (6.36 g, 6.5 mL, 0.10 mol, 4 eq.) was added dropwise, taking care to not allow the temperature to exceed 20 °C. The mixture was then heated to 60 °C for 90 min and after cooling, poured into ice water. Resulting precipitate was filtered, washed several times with acetic acid and toluene then dried under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/AcOEt: 8/2) to provide a yellowish solid, m.p. 213 °C (3.82 g, 13.3 mmol, 53 % yield). ¹H NMR (DMSO d₆) δ(ppm): 9.08 (s, 2H), 9.82 (s, 2H); ¹³C NMR (DMSO d₆) δ(ppm): 122.1 (C_q), 127.0 (CH_{Ar}), 130.6 (C_q), 132.2 (CH_{Ar}), 133.6 (C_q), 147.1 (C_q), 158.8 (C=O); HRMS (ESI MS) m/z: theor: 306.0357 found: 306.0358 ((M+NH₄)⁺ detected).

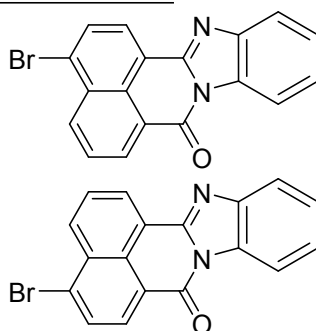
N-((dimethylamino)ethyl)-3,6-dinitro-1,8-naphthalimide (DNND2)



C₁₆H₁₄N₄O₆
 MW = 358.31 g.mol⁻¹
 Exact Mass: 358.0913

A mixture of 3,6-dinitro-1,8-naphthalic anhydride (1.0 g, 3.47 mmol) and N,N-dimethylethylenediamine (0.40 mL, 3.64 mmol, 1.05 eq.) in ethanol (50 mL) was refluxed for 2.5 hours. Obtained solution was cooled with an ice/water bath. Then resulting precipitate was filtered, washed several times with ethanol and pentane to afford a compound as a brown solid, m.p. 218 °C (611 mg, 1.7 mmol, 49 % yield). ¹H NMR (DMSO d₆) δ(ppm): 2.24 (s, 6H), 2.58 (t, 2H, J = 6.4 Hz), 4.19 (t, 2H, J = 6.7 Hz), 9.06 (d, 2H, J = 1.8 Hz), 9.74 (d, 2H, J = 1.5 Hz); ¹³C NMR (DMSO d₆) δ(ppm): 38.1 (CH₂), 45.2 (CH₃), 56.1 (CH₂), 124.4 (C_q), 125.9 (CH_{Ar}), 130.7 (C_q), 131.4 (CH_{Ar}), 131.5 (C_q), 147.1 (C_q), 161.7 (C=O); HRMS (ESI MS) m/z: theor: 359.0986 found: 359.0987 ((M+H)⁺ detected).

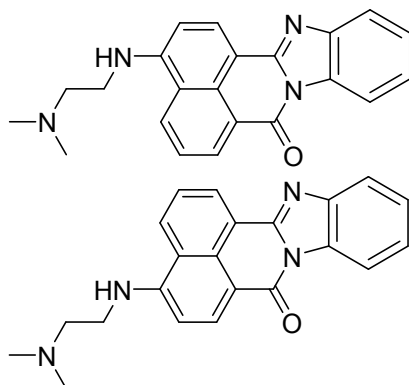
3-Bromo-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one and 4-Bromo-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one



C₁₈H₉BrN₂O
 MW = 349.18 g.mol⁻¹
 Exact Mass: 347.9898

A mixture of 4-Bromo-1,8-naphthalic anhydride (1.0 g, 3.61 mmol) and o-Phenylenediamine (468 mg, 4.33 mmol, 1.2 eq.) in acetic acid (20 mL) was refluxed for 24 h. . Obtained solution was cooled with an ice/water bath. Then resulting precipitate was filtered, washed several times with ethanol and pentane to afford a compound as a yellow solid under the form of a mixture of isomers, m.p. 247 °C (1.05 g, 3.01 mmol, 83 % yield). ¹H NMR (CDCl₃) δ(ppm): 7.50 (m, 4H), 7.90 (m, 4H), 8.08 (d, 1H, J = 8.1 Hz), 8.10 (d, 1H, J = 8.6 Hz), 8.52 (m, 3H), 8.58 (d, 1H, J = 7.8 Hz), 8.65 (d, 1H, J = 7.5 Hz), 8.66 (d, 1H, J = 8.1 Hz), 8.83 (d, 1H, J = 7.2 Hz), 8.89 (d, 1H, J = 7.0 Hz); ¹³C NMR (CDCl₃) δ(ppm): 115.9 (CH_{Ar}), 119.9 (CH_{Ar}), 120.0 (CH_{Ar}), 120.1 (C_q), 120.9 (C_q), 122.7 (C_q), 123.6 (C_q), 125.8 (CH_{Ar}), 126.09 (CH_{Ar}), 126.11 (CH_{Ar}), 127.3 (CH_{Ar}), 127.8 (C_q), 128.0 (C_q), 128.1 (CH_{Ar}), 128.2 (CH_{Ar}), 128.6 (CH_{Ar}), 129.2 (C_q), 131.2 (CH_{Ar}), 131.3 (C_q), 131.4 (CH_{Ar}), 131.6 (CH_{Ar}), 131.7 (CH_{Ar}), 132.0 (C_q), 132.5 (CH_{Ar}), 133.3 (C_q), 134.7 (CH_{Ar}), 135.2 (C_q), 143.3 (C_q), 148.7 (C_q), 160.0 (C=O); HRMS (ESI MS) m/z: theor: 348.9971 found: 348.9972 ((M+H)⁺ detected)

3-(N-((dimethylamino)ethyl)-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one and 4-(N-((di-methylamino)ethyl)-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one (DNND5)

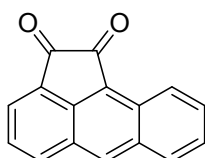


C₂₂H₂₀N₄O
 MW = 356.42 g.mol⁻¹
 Exact Mass: 356.1637

A mixture of 3 and 4-Bromo-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one (0.5 g, 1.43 mmol), N,N-dimethylethylenediamine (1.25 mL, 11.46 mmol, 8 eq.) and cupric sulfate pentahydrate (54.9 mg, 0.22 mmol) in 2-ethoxyethanol (15 mL) was refluxed for 6h. After cooling, the solution was poured onto water (30 mL) and then extracted with CHCl₃ (3*50 mL). The combined organic layers were washed with water (3*25 mL), dried over MgSO₄ and concentrated. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/MeOH/Et₃N: 9/1/0.1) to provide a red solid under the form of a mixture of isomers, m.p. 204 °C (373 mg, 1.05 mmol, 73 % yield). ¹H NMR (CDCl₃) δ(ppm): 2.35 (s, 12H), 2.73 (t, 4H, J = 5.8 Hz), 3.38 (dt, 4H, ²J = 10.8 Hz, ³J = 5.0 Hz), 6.19 (bs, 1H), 6.46 (bs, 1H), 6.70 (d, 1H, J = 8.5 Hz), 6.73 (d, 1H, J = 8.5 Hz), 7.40 (t, 1H, J = 7.7 Hz), 7.46 (m, 3H), 7.68 (t, 1H, J = 7.8 Hz), 7.73 (d, 1H, J = 7.5 Hz), 7.82 (d, 1H, J = 7.8 Hz), 7.89 (m, 1H), 8.05 (d, 1H, J = 8.5 Hz), 8.26 (d, 1H, J = 8.3 Hz), 8.56 (d, 1H, J = 7.5 Hz), 8.62 (m, 2H), 8.68 (d, 1H, J = 8.3 Hz), 8.80 (d, 1H, J = 7.3 Hz), 8.85 (d, 1H, J = 7.3 Hz); ¹³C NMR (CDCl₃) δ(ppm): 40.1 (CH₂), 40.3 (CH₂), 45.03 (CH₃), 45.06 (CH₃), 56.8 (CH₂), 57.0 (CH₂), 104.7 (CH_{Ar}), 105.2 (CH_{Ar}), 110.2 (C_q), 115.7 (CH_{Ar}), 116.0 (CH_{Ar}), 118.8 (CH_{Ar}), 119.5 (CH_{Ar}), 120.75 (C_q),

120.78 (C_q), 123.7 (CH_{Ar}), 124.0 (CH_{Ar}), 124.58 (CH_{Ar}), 124.63 (CH_{Ar}), 125.0 (CH_{Ar}), 125.1 (CH_{Ar}), 125.4 (CH_{Ar}), 127.1 (CH_{Ar}), 127.6 (CH_{Ar}), 128.7 (C_q), 130.5 (CH_{Ar}), 131.6 (CH_{Ar}), 132.1 (C_q), 135.3 (CH_{Ar}), 143.8 (C_q), 148.4 (C_q), 150.6 (C_q), 160.9 (C=O); HRMS (ESI MS) m/z: theor: 357.1710 found: 357.1709 ((M+H)⁺ detected).

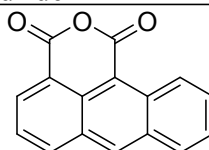
Aceanthrylene-1,2-dione



C₁₆H₈O₂
MW = 232.23 g.mol⁻¹
Exact Mass: 232.0524

A solution of oxalyl chloride (10.8 mL, 0.12 mol, 5.5 eq.) and anthracene (4.0 g, 22.4 mmol) was introduced in 250 mL two-neck flask, under an N₂ atmosphere, containing carbon disulfide (48 mL) then the mixture was cooled at 0 °C in ice bath. Anhydrous AlCl₃ (4.8 g, 36.0 mmol, 1.6 eq.) was added then after 2 h, additional carbon disulfide (48 mL) and anhydrous AlCl₃ (3.6 g, 27.0 mmol, 1.2 eq.) were added, and stirring was continued for another 2 h at 0 °C and then overnight at room temperature. Dilute aqueous HCl (2 M) was added and the orange precipitate formed was collected by filtration, washed with water, treated with 200 mL of 5% NaOH, still washed with water and dried under vacuum to provide an orange solid, m.p. 260 °C (3.65 g, 15.7 mmol, 70 %). ¹H NMR (CDCl₃) δ(ppm): 7.72 (t, 1H, J = 7.3 Hz), 7.78 (t, 1H, J = 7.7 Hz), 7.85 (t, 1H, J = 7.3 Hz), 8.07 (d, 1H, J = 6.3 Hz), 8.20 (d, 1H, J = 8.5 Hz), 8.34 (d, 1H, J = 8.5 Hz), 8.87 (s, 1H), 9.15 (d, 1H, J = 8.3 Hz); ¹³C NMR (CDCl₃) δ(ppm): 121.7 (CH_{Ar}), 123.2 (C_q), 124.7 (CH_{Ar}), 127.3 (CH_{Ar}), 127.5 (C_q), 127.6 (CH_{Ar}), 128.0 (C_q), 128.2 (C_q), 129.5 (CH_{Ar}), 130.5 (CH_{Ar}), 132.3 (CH_{Ar}), 132.9 (C_q), 134.0 (CH_{Ar}), 147.0 (C_q), 187.6 (C=O), 189.1 (C=O); HRMS (ESI MS) m/z: theor: 233.0597 found: 233.0598 ((M+H)⁺ detected).

Anthracene-1,2-dicarboxylic acid anhydride

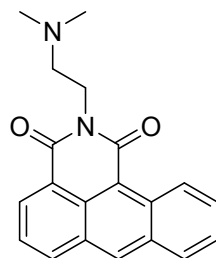


C₁₆H₈O₃
MW = 248.23 g.mol⁻¹
Exact Mass: 248.0473

A mixture of aceanthrylene-1,2-dione (3.0 g, 12.9 mmol) and oxone (15.9 g, 25.8 mmol, 2 eq.) in methanol (430 mL) was refluxed for 72 hours. After cooling, water was added and the resulting precipitate was filtered, washed several times with water and ethanol then dried under vacuum to provide an orange solid, m.p. 295 °C (2.2 g, 8.86 mmol, 69 %). ¹H NMR (CDCl₃) δ(ppm): 7.74 (t, 1H, J = 7.4 Hz), 7.82 (t, 1H, J = 7.7 Hz), 7.94 (t, 1H, J = 7.4 Hz),

8.21 (d, 1H, J = 8.5 Hz), 8.50 (d, 1H, J = 8.0 Hz), 8.80 (d, 1H, J = 6.8 Hz), 8.99 (s, 1H), 9.77 (d, 1H, J = 9.2 Hz); ^{13}C NMR (CDCl_3) δ (ppm): 125.8 (CH_{Ar}), 126.3 (CH_{Ar}), 127.2 (CH_{Ar}), 130.0 (CH_{Ar}), 132.3 (CH_{Ar}), 135.7 (CH_{Ar}), 136.5 (CH_{Ar}), 137.9 (CH_{Ar}); HRMS (ESI MS) m/z: theor: 249.0546 found: 249.0544 ((M+H)⁺ detected).

N-((dimethylamino)ethyl)-anthracene carboximide (DNND4)



$\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2$
MW = 318.37 g.mol⁻¹
Exact Mass: 318.1368

A mixture of anthracene-1,2-dicarboxylic acid anhydride (0.3 g, 1.21 mmol) and N,N-dimethylethylenediamine (0.14 mL, 1.33 mmol, 1.1 eq.) in ethanol (5 mL) was refluxed for 2h30. After cooling, the solution was poured onto water and then extracted with CH_2Cl_2 . The crude product was purified by column chromatography on silica gel (CH_2Cl_2 /Ethanol: 9/1) to afford an orange solid, m.p. 126 °C (228 mg, 0.72 mmol, 59 % yield). ^1H NMR (CDCl_3) δ (ppm): 2.42 (s, 6H), 2.74 (t, 2H, J = 7.2 Hz), 4.43 (t, 2H, J = 7.2 Hz), 7.61 (t, 1H, J = 7.3 Hz), 7.69 (dd, 1H, ^3J = 7.8 Hz, ^3J = 7.3 Hz), 7.81 (ddd, 1H, ^3J = 8.8 Hz, ^3J = 6.6 Hz, ^4J = 1.3 Hz), 8.07 (d, 1H, J = 8.3 Hz), 8.30 (d, 1H, J = 8.3 Hz), 8.71 (dd, 1H, ^3J = 7.0 Hz, ^4J = 1.0 Hz), 8.76 (s, 1H), 9.96 (d, 1H, J = 9.0 Hz); ^{13}C NMR (CDCl_3) δ (ppm): 38.3 (CH_2), 45.8 (CH_3), 57.0 (CH_2), 115.2 (C_q), 122.4 (C_q), 125.3 (CH_{Ar}), 126.4 (CH_{Ar}), 126.7 (CH_{Ar}), 128.3 (C_q), 128.7 (C_q), 129.6 (CH_{Ar}), 131.2 (CH_{Ar}), 132.3 (C_q), 133.39 (CH_{Ar}), 133.44 (C_q), 135.0 (CH_{Ar}), 136.2 (CH_{Ar}), 163.6 (C=O), 165.0 (C=O); HRMS (ESI MS) m/z: theor: 319.1441 found: 319.1439 ((M+H)⁺ detected).

Preparation of the DNND4@SBE- β -CD complex

An equimolar quantity (3.14×10^{-5} mol) of DNND4 (10.0 mg) and sulfobutylether- β -cyclodextrin (SBE- β -CD), 68.4 mg which was a generous gift from Clemens Glaubitz (Institute for Biophysical Chemistry, Goethe University Frankfurt, Germany) was weighted in a 1.5 mL Eppendorf vial before adding 1 mL of HPLC grade water. The mixture was then sonicated for 2 minutes before filtration and freeze-drying affording 58 mg of the inclusion complex as a cotton-like yellowish solid.

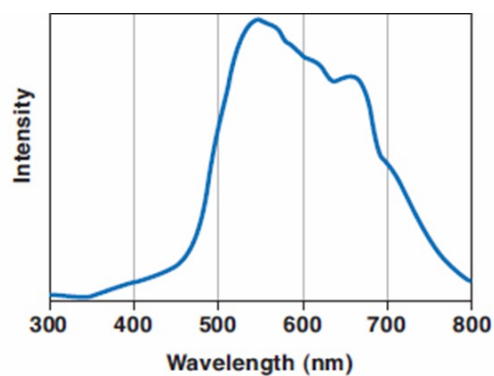


Figure S1. The emission spectrum of the halogen lamp.

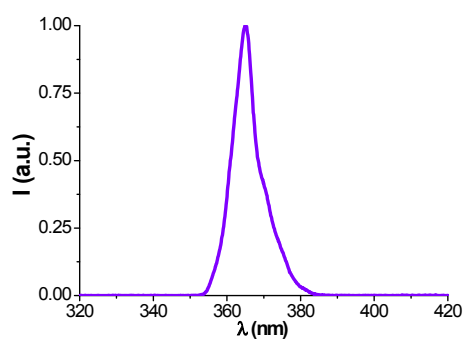


Figure S2. The emission spectrum of the LED centered at 365 nm.

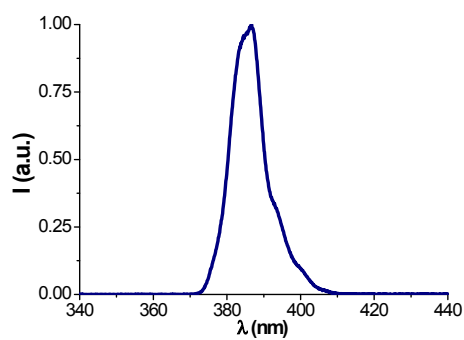


Figure S3. The emission spectrum of the LED centered at 385 nm.

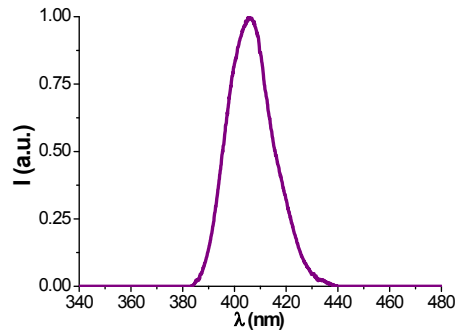


Figure S4. The emission spectrum of the LED centered at 405 nm*.

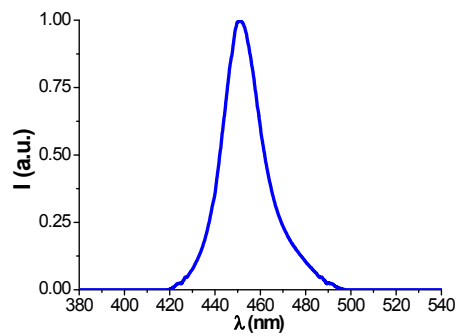


Figure S5. The emission spectrum of the blue LED centered at 455 nm*.

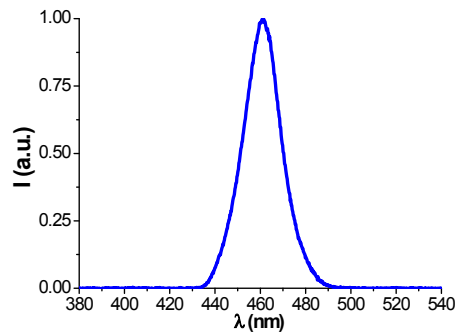


Figure S6. The emission spectrum of the blue LED centered at 470 nm*.

*For Figures S2-S6, the nominal wavelengths indicate the wavelengths at which the LEDs appear brightest to the human eye. This may not correspond to the peak wavelength as measured by a spectrograph. (from <http://www.thorlabs.de/>)

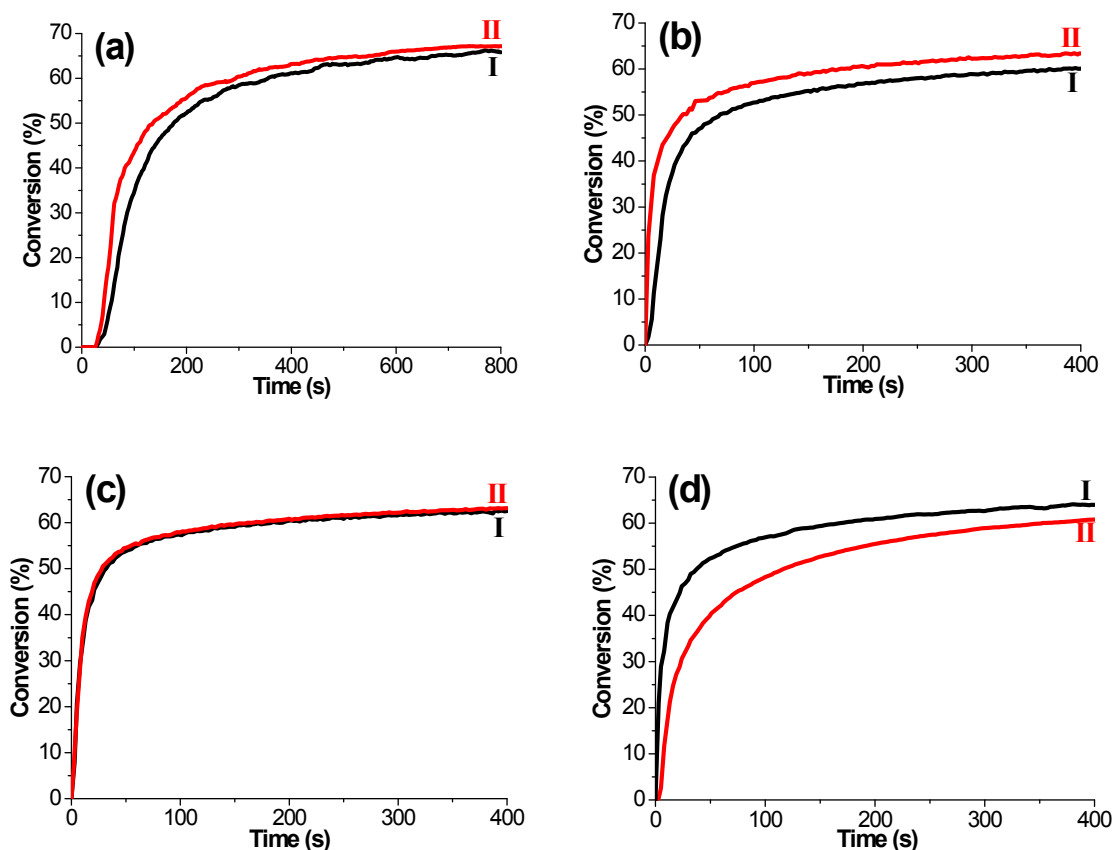


Figure S7. Photopolymerization profiles of (a) EPOX under air in the presence of DNND3/Iod upon the LED at 405 nm exposure; and of TMPTA in laminate in the presence of (b) DNND3/R-Cl, (c) DNND3/Iod/NVK upon the LED at 405 nm exposure and (d) DNND5/MDEA/R-Cl upon the LED at 455 nm exposure; curve I - measured from freshly prepared formulations, curve II - measured after one week of storage at room temperature. [Note: In (a) and (b), the photoinitiating ability of the relevant PISs was a little higher after one week of storage. It indicated that i) the formulations were stable as the photopolymerization efficiency was not decreased after one week and ii) the environment change (*e.g.* moisture of the atmosphere and the difference of temperature) did not significantly affect the efficiency of cationic photopolymerization and free radical photopolymerization *i.e.* only led to a little improvement of final conversion (< 5%).]

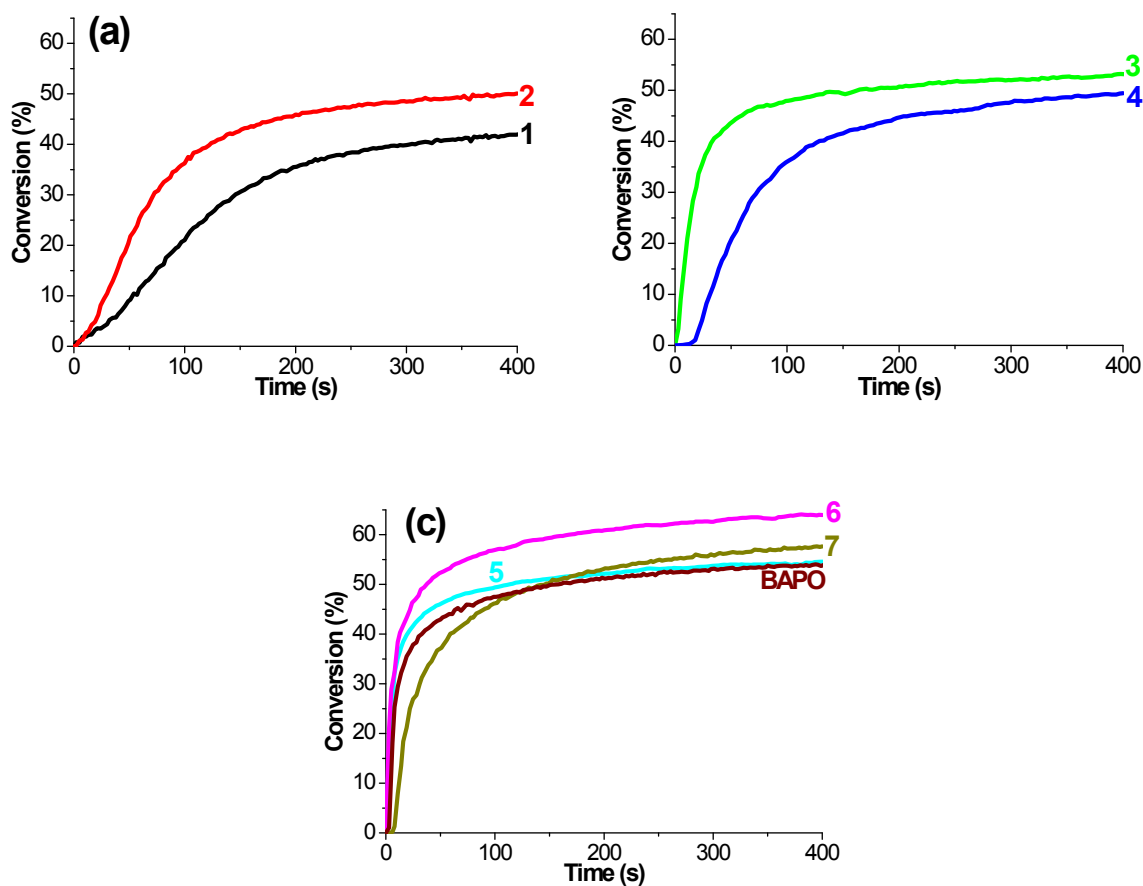


Figure S8. Photopolymerization profiles of TMPTA (acrylate function conversion vs. time) in laminate in the presence of DNNDs based PISs: (a) DNND1/R-Cl (curve 1) or DNND3/Iod (curve 2) upon the exposure to LED at 385 nm; (b) DNND3/Iod (curve 3), DNND4/Iod/NVK (curve 4); and (c) DNND5/R-Cl (curve 5) or DNND5/MDEA/R-Cl (curve 6) upon the exposure to LED at 455 nm; DNND5/MDEA/R-Cl upon the exposure to LED at 470 nm (curve 7). BAPO (0.5 wt%) upon the LED at 455 nm exposure as a reference; DNNDs: 0.5 wt%; Iod or MDEA: 2 wt%; NVK or R-Cl: 3wt% in the formulations.

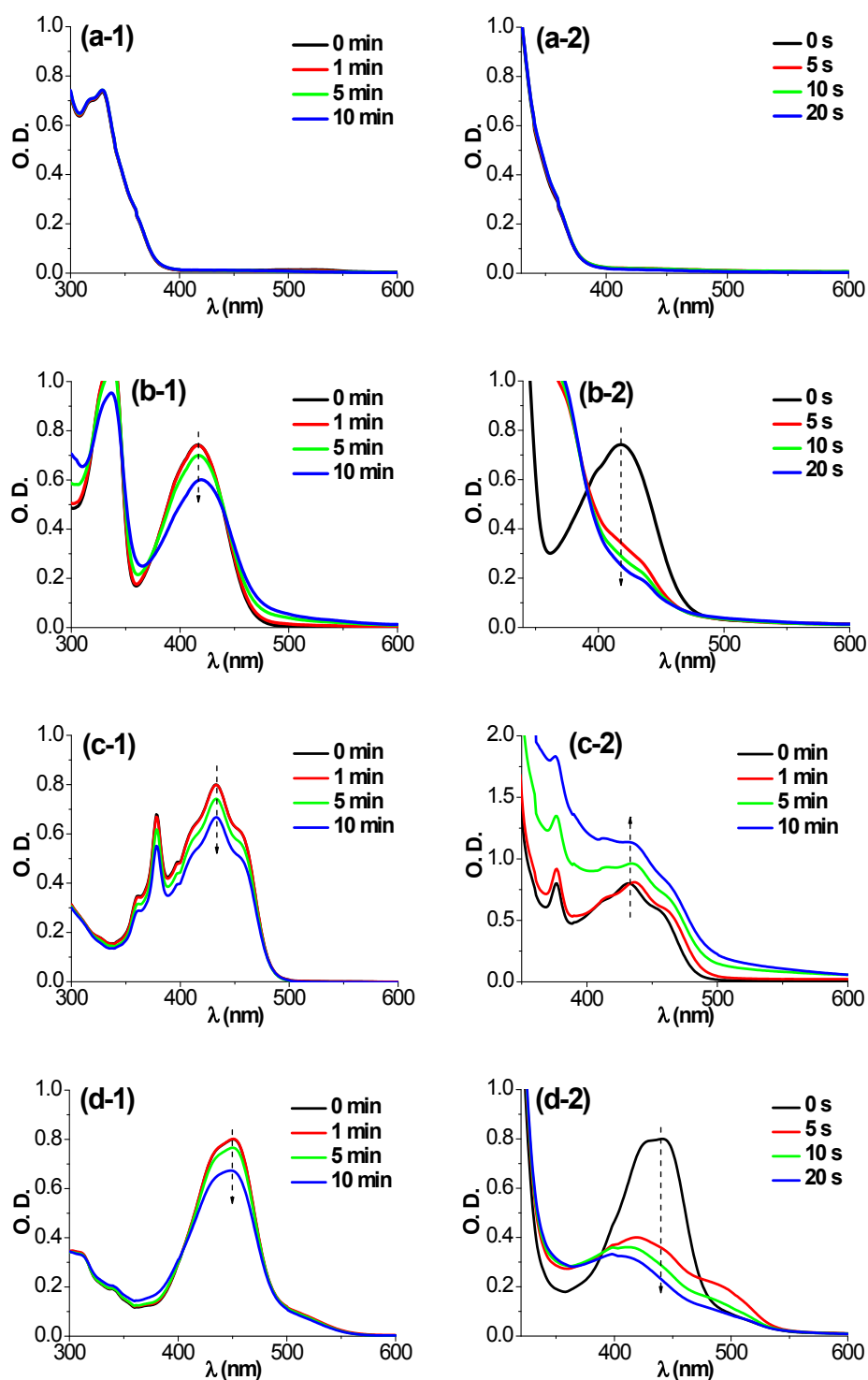
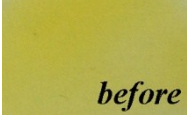
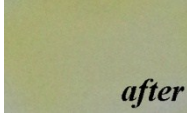

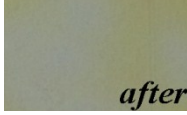


Figure S9. Steady state photolysis of DNNDs alone or DNNDs/additive in acetonitrile ($[Iod] = [R-Cl] = 15 \text{ mM}$, $[EDB] = 35 \text{ mM}$) upon the LED exposure at 405 nm: (a-1) DNND1, (a-2) DNND1/R-Cl, (b-1) DNND3, (b-2) DNND3/R-Cl, (c-1) DNND4, (c-2) DNND4/Iod/EDB, (d-1) DNND5 and (d-2) DNND5/R-Cl; UV-vis spectra recorded at different irradiation times.

Table S1. Color change of TMPTA or EPOX/TMPTA (50%/50%, w/w) film after photopolymerization in laminate in the presence of DNND4 based PIS upon the LED at 405 nm exposure.

PIS (monomer)	Film color before and after the polymerization	
DNND4/Iod (TMPTA)	 <p style="text-align: center;"><i>before</i></p>	 <p style="text-align: center;"><i>after</i></p>
DNND4/Iod/NVK (EPOX/TMPTA, 50%/50%, w/w)	 <p style="text-align: center;"><i>before</i></p>	 <p style="text-align: center;"><i>after</i></p>