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# **Supporting Information:**

# *N*-[2-(dimethylamino)ethyl]-1,8-naphthalimide Derivatives as Photoinitiators under LEDs

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## Synthesis of ANNs



Scheme S1. Chemical structures of investigated photoinitiators ANNs in this study.

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined at room temperature in 5 mm o.d.

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tubes on a Bruker Avance 400 spectrometer of the Spectropole: <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz). The <sup>1</sup>H chemical shifts were referenced to the solvent peaks CDCl<sub>3</sub> (7.26 ppm), DMSO (2.49 ppm) and the <sup>13</sup>C chemical shifts were referenced to the solvent peaks CDCl<sub>3</sub> (77 ppm), DMSO (49.5 ppm). All these carbazole photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.



Scheme S2. Synthetic pathways to ANN0-ANN3

Synthesis of 4-bromo-N-((dimethylamino)ethyl)-1,8-naphthalimide ANN0.



A mixture of 4-bromo-1,8-naphthalic anhydride (2.0 g, 7.22 mmol, M = 277.07 g/mol) and *N*,*N*-dimethylethylenediamine (0.67 g, 0.82 mL, 7.58 mmol, 1.05 eq., M = 88.15 g/mol, d = 0.810) in ethanol (20 mL) was stirred at reflux temperature for 2 h 30. The solution was slowly cooled; once at room temperature, the formation of a yellow precipitate was observed. The precipitate was collected by filtration, washed with ethanol and pentane. The desired molecule was obtained as light yellow solid (1.96 g, 5.65 mmol, 78 % yield). *<sup>1</sup>H NMR (CDCl<sub>3</sub>)*  $\delta$ (*ppm*):

2.36 (s, 6H), 2.66 (t, 2H,  ${}^{3}J = 7.0 \text{ Hz}$ ), 4.33 (t, 2H,  ${}^{3}J = 6.9 \text{ Hz}$ ), 7.85 (t, 1H,  ${}^{3}J = 7.9 \text{ Hz}$ ), 8.05 (d, 1H,  ${}^{3}J = 7.8 \text{ Hz}$ ), 8.42 (d, 1H,  ${}^{3}J = 8.0 \text{ Hz}$ ), 8.58 (d, 1H,  ${}^{3}J = 8.5 \text{ Hz}$ ), 8.67 (d, 1H,  ${}^{3}J = 7.3 \text{ Hz}$ );  ${}^{13}C$  *NMR (CDCl<sub>3</sub>)*  $\delta(ppm)$ : 38.3 (CH<sub>2</sub>), 45.8 (CH<sub>3</sub>), 56.9 (CH<sub>2</sub>), 122.2 (C<sub>q</sub>), 123.1 (C<sub>q</sub>), 128.1 (CH), 129.1 (C<sub>q</sub>), 130.3 (C<sub>q</sub>), 130.6 (C<sub>q</sub>), 131.1 (CH), 131.3 (CH), 132.1 (CH), 133.3 (CH), 163.65 (C=O), 163.67 (C=O); *HRMS (ESI MS) m/z*: theor: 347.0390 found: 347.0389 ((M+H)<sup>+</sup> detected).

#### 4-Nitro-1,8-napthalic acid anhydride (1).



Sodium dichromate dihydrate (13.46 g, 45.18 mmol, 2.5 eq., M = 298.0 g/mol) was introduced in a solution of concentrated acetic acid (30 mL). 5-Nitroacenaphthene (3.6 g, 18.07 mmol, M = 199.21 g/mol) in concentrated acetic acid (30 mL) was added dropwise and the mixture was stirred at reflux temperature for 5 h. After cooling to 0 °C, the crude was precipitate by addition

of cold water (300 mL). The precipitate was collected by filtration, washed with water, and dried under vacuum. The crude product was purified by a washing with a melt of a solution of CH<sub>2</sub>Cl<sub>2</sub>/pentane (1/1) (2.68 g, 11.02 mmol, 61 % yield). <sup>1</sup>*H NMR (DMSO-d<sub>6</sub>) \delta(ppm)*: 8.12 (t, 1H, <sup>3</sup>J = 8.0 Hz), 8.56 (d, 1H, <sup>3</sup>J = 8.0 Hz), 8.63 (d, 1H, <sup>3</sup>J = 8.0 Hz), 8.66 (d, 1H, <sup>3</sup>J = 7.3 Hz), 8.76 (d, 1H, <sup>3</sup>J = 8.5 Hz); <sup>13</sup>*C NMR (DMSO-d<sub>6</sub>) \delta(ppm)*: 120.1 (C<sub>q</sub>), 122.8 (C<sub>q</sub>), 124.1 (C<sub>q</sub>), 124.4 (CH), 129.8 (CH), 130.3 (CH), 130.6 (C<sub>q</sub>), 131.1 (CH), 133.2 (CH), 149.6 (C<sub>q</sub>), 159.5 (C=O), 160.1 (C=O); *HRMS (ESI MS) m/z*: theor: 244.0240 found: 244.0239 ((M+H)<sup>+</sup> detected).

#### 4-Amino-1,8-napthalic acid anhydride (2).



Tin (II) chloride (9.65 g, 42.77 mmol, 5.2 eq., M = 225.65 g/mol) in concentrated HCl (7 mL) was added dropwise to the solution of 4-nitro-1,8-napthalic acid anhydride (2.0 g, 8.22 mmol, M = 243.17 g/mol) in ethanol (4 mL). The mixture was heated at reflux of ethanol for 2 h. The solution was slowly cooled; once at

room temperature, the formation of a yellow precipitate was observed. The precipitate was collected by filtration, washed with water, ethanol and pentane. The desired molecule was obtained as orange solid (1.15 g, 5.39 mmol, 66 % yield). <sup>1</sup>*H NMR (DMSO-d<sub>6</sub>) \delta(ppm)*: 6.87 (d, 1H, <sup>3</sup>J = 8.5 Hz), 7.68 (t, 1H, <sup>3</sup>J = 7.8 Hz), 7.78 (bs, 2H), 8.17 (d, 1H, <sup>3</sup>J = 8.5 Hz), 8.42 (d, 1H, <sup>3</sup>J = 7.0 Hz), 8.67 (d, 1H, <sup>3</sup>J = 8.3 Hz); <sup>13</sup>*C NMR (DMSO-d<sub>6</sub>) \delta(ppm)*: 102.2 (C<sub>q</sub>), 108.7 (CH), 118.3 (C<sub>q</sub>), 119.3 (C<sub>q</sub>), 124.4 (CH), 130.7 (CH), 132.6 (C<sub>q</sub>), 133.0 (CH), 135.9 (CH), 153.9 (C<sub>q</sub>), 160.3 (C=O), 162.0 (C=O); *HRMS (ESI MS) m/z*: theor: 214.0499 found: 214.0497 ((M+H)<sup>+</sup> detected).

#### Synthesis of *N*-((dimethylamino)ethyl)-4-(amino)-1,8-naphthalimide ANN1.



A mixture of 4-amino-1,8-naphthalic acid anhydride (700 mg, 3.28 mmol, M = 213.19 g/mol) and *N*,*N*-dimethylethylenediamine (304 mg, 0.38 mL, 3.45 mmol, 1.05 eq., M = 88.15 g/mol, d = 0.810) in ethanol (20 mL) was stirred at reflux temperature for 5 h. After cooling to room temperature, the solution was filtered on silica thin layer. The solvent was removed using a rotary evaporator under reduced pressure to afford the pure product as orange solid (812 mg, 2.87 mmol,

87 % yield). <sup>1</sup>*H* NMR (CDCl<sub>3</sub>) δ(ppm): 2.41 (s, 6H), 2.73 (t, 2H, <sup>3</sup>J = 6.9 Hz), 4.34 (t, 2H, <sup>3</sup>J = 6.9 Hz), 5.11 (bs, 2H), 6.77 (d, 1H, <sup>3</sup>J = 8.0 Hz), 7.61 (t, 1H, <sup>3</sup>J = 7.9 Hz), 8.04 (d, 1H, <sup>3</sup>J = 8.3 Hz), 8.32 (d, 1H, <sup>3</sup>J = 8.0 Hz), 8.56 (d, 1H, <sup>3</sup>J = 7.3 Hz); <sup>13</sup>*C* NMR (CDCl<sub>3</sub>) δ(ppm): 37.7 (CH<sub>2</sub>), 45.6 (CH<sub>3</sub>), 57.1 (CH<sub>2</sub>), 109.5 (CH), 111.9 (C<sub>q</sub>), 120.0 (C<sub>q</sub>), 124.9 (CH), 126.8 (CH), 131.5 (CH), 133.8 (CH), 149.2 (C<sub>q</sub>), 164.0 (C=O), 164.7 (C=O); *HRMS (ESI MS) m/z*: theor: 284.1394 found: 284.1395 ((M+H)<sup>+</sup> detected).

# Synthesis of *N*-((dimethylamino)ethyl)-4-(hexylamino)-1,8-naphthalimide ANN2.



A mixture of 4-bromo-*N*-((dimethylamino)ethyl)-1,8-naphthalimide (0.5 g, 1.44 mmol, M = 347.21 g/mol) and hexylamine (0.44 g, 0.57 mL, 4.32 mmol, 3 eq., M = 101.19 g/mol, d = 0.773) in 2-ethoxyethanol (5 mL) was stirred at reflux temperature for 16 h. After cooling to room temperature, the solution was concentrated under reduced pressure until most of the solvent was removed. The residue was poured into the water (30 mL) and extracted with CHCl<sub>3</sub> (3×50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and

concentrated. The crude product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 25/1 to 10/1) to provide a yellow solid (403 mg, 1.1 mmol, 76 % yield). <sup>*I*</sup>*H NMR* (*CDCl*<sub>3</sub>)  $\delta$ (*ppm*): 0.93 (t, 3H, J = 7.0 Hz), 1.38 (m, 4H), 1.50 (m, 2H), 1.81 (quint, 2H, <sup>3</sup>J

= 7.3 Hz), 2.37 (s, 6H), 2.66 (t, 2H,  ${}^{3}J$  = 7.2 Hz), 3.40 (m, 2H), 4.32 (t, 2H,  ${}^{3}J$  = 7.2 Hz), 5.31 (bs, 1H), 6.69 (t, 1H,  ${}^{3}J$  = 8.3 Hz), 7.59 (t, 1H,  ${}^{3}J$  = 7.8 Hz), 8.07 (d, 1H,  ${}^{3}J$  = 8.3 Hz), 8.43 (d, 1H,  ${}^{3}J$  = 8.3 Hz), 8.55 (d, 1H,  ${}^{3}J$  = 7.3 Hz);  ${}^{13}C$  *NMR (CDCl<sub>3</sub>)*  $\delta$ (*ppm*): 14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 26.8 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 43.7 (CH<sub>2</sub>), 45.7 (CH<sub>3</sub>), 57.1 (CH<sub>2</sub>), 104.3 (CH), 110.0 (C<sub>q</sub>), 120.1 (C<sub>q</sub>), 123.0 (C<sub>q</sub>), 124.6 (CH), 125.8 (CH), 129.8 (C<sub>q</sub>), 131.1 (CH), 134.5 (CH), 149.5 (C<sub>q</sub>), 164.1 (C=O), 164.7 (C=O); *HRMS (ESI MS) m/z*: theor: 368.2333 found: 368.2335 ((M+H)<sup>+</sup> detected).

## Synthesis of *N*-((dimethylamino)ethyl)-4-(piperidine)-1,8-naphthalimide ANN3.



A mixture of 4-bromo-*N*-((dimethylamino)ethyl)-1,8-naphthalimide (950 mg, 2.74 mmol, M = 347.21 g/mol) and piperidine (0.70 g, 0.81 mL, 8.21 mmol, 3 eq., M = 85.15 g/mol, d = 0.861) in 2-ethoxyethanol (10 mL) was stirred at reflux for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1) to provide an orange solid as pure product (791 mg, 2.25 mmol, 82 % yield). <sup>*1*</sup>*H NMR (CDCl<sub>3</sub>)*  $\delta(ppm)$ : 1.71 (m, 2H), 1.88 (m,

4H), 2.36 (s, 6H), 2.64 (t, 2H,  ${}^{3}J = 7.2 \text{ Hz}$ ), 3.21 (m, 4H), 4.31 (t, 2H,  ${}^{3}J = 7.2 \text{ Hz}$ ), 7.16 (d, 1H,  ${}^{3}J = 8.0 \text{ Hz}$ ), 7.66 (t, 1H,  ${}^{3}J = 7.8 \text{ Hz}$ ), 8.37 (d, 1H,  ${}^{3}J = 8.3 \text{ Hz}$ ), 8.47 (d, 1H,  ${}^{3}J = 8.0 \text{ Hz}$ ), 8.55 (d, 1H,  ${}^{3}J = 7.0 \text{ Hz}$ );  ${}^{13}C NMR (CDCl_3) \delta(ppm)$ : 24.3 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 37.9 (CH<sub>2</sub>), 45.7 (CH<sub>3</sub>), 54.5 (CH<sub>2</sub>), 57.0 (CH<sub>2</sub>), 114.6 (CH), 115.8 (C<sub>q</sub>), 123.0 (C<sub>q</sub>), 125.3 (CH), 126.2 (C<sub>q</sub>), 129.9 (C<sub>q</sub>), 130.6 (CH), 131.0 (CH), 132.6 (CH), 157.3 (C<sub>q</sub>), 164.1 (C=O), 164.6 (C=O); *HRMS (ESI MS) m/z*: theor: 352.2020 found: 352.2019 ((M+H)<sup>+</sup> detected).



Figure S1. The emission spectra of the LEDs used in this study\*.

\*For Figure S1, 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 <u>http://www.thorlabs.de/</u>)



Figure S2. The emission spectrum of the halogen lamp.



**Figure S3.** Photopolymerization profiles of TMPTA under air in the presence of ANN1/Iod/NVK (0.5 wt%/2 wt%/3 wt%) upon the LED at 405 nm (curve 1) or 455 nm (curve 2) exposure; BAPO (0.5 wt%) under LED at 405 nm as reference.



**Figure S4**. Photopolymerization profiles of (a) EPOX under air in the presence of ANN2/Iod/NVK upon the LED at 455 nm exposure; and of TMPTA in laminate in the presence of (b) ANN2/Iod/NVK, (c) ANN2/R-Cl and (d) ANN3/R-Cl upon the LED at 405 nm exposure; curve I - measured from freshly prepared formulations, curve II - measured after one week of storage at room temperature.



**Figure S5.** Picture of a square of polymer (length: 10 mm; width: 6 mm; thickness 1 mm) obtained from 3D printing of triethylene glycol diacrylate/EPOX (50%/50% w/w) blend under air using ANN2/Iod (0.5%/2% w/w) as a photoinitiating system; 3D printer (ProJet 1200 from 3D systems).



**Figure S6.** Steady state photolysis of (a) ANN1; (b) ANN2; and (c) ANN3 in acetonitrile upon the LED at 405 nm exposure; UV-vis spectra recorded at different irradiation time.