

Electronic Supplementary Information

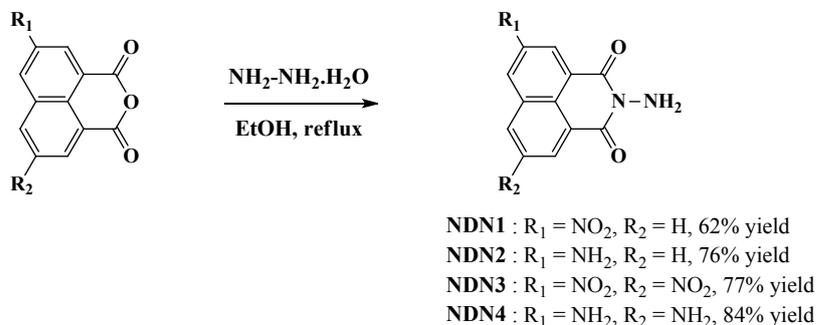
Amino and Nitro Substituted 2-Amino-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-diones: as Versatile Photoinitiators of Polymerization From Violet-Blue LEDs Absorption to a Panchromatic Behavior.

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and Jacques Lalevée

Syntheses of 2-amino-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione derivatives (NDNs)

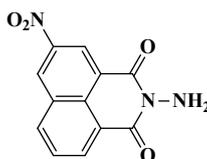
All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. ¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peak DMSO (2.49 ppm) and the ¹³C chemical shifts were referenced to the solvent peak DMSO (49.5 ppm). All these dyes were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. 5-Nitrobenzo[*de*]isochromene-1,3-dione [J.-J. Lee, B. C. Noll, B. D. Smith, *Org. Lett.*, 2008, 10, 1735–1738], 5-Aminobenzo[*de*]isochromene-1,3-dione [L. K. E. Hardebeck, C. A. Johnson, G. A. Hudson, Y. Ren, M. Watt, C. C. Kirkpatrick, B. M. Znosko, M. Lewis, *J. Phys. Org. Chem.* 2013, 26 879–884], 5,8-dinitrobenzo[*de*]isochromene-1,3-dione [S. Girouard, M.-H. Houle, A. Grandbois, J. W. Keillor, S. W. Michnick, *J. Am. Chem. Soc.*, 2005, 127, 559–566] and 5,8-diaminobenzo[*de*]isochromene-1,3-dione [A. Peduto, B. Pagano, C. Petronzi, A. Massa, V.

Esposito, A. Virgilio, F. Paduano, F. Trapasso, F. Fiorito, S. Florio, C. Giancola, A. Galeone, R. Filosa, *Biol. Med. Chem.* 2011, 19, 6419–6429] were synthesized according to literature procedure, without modifications and in similar yields.



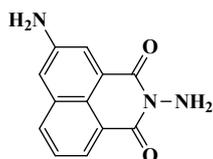
Synthetic route to **NDN1-NDN4**

Synthesis of 2-amino-5-nitro-1H-benzo[de]isoquinoline-1,3(2H)-dione (NDN1)



3-Nitro-1,8-naphthalic acid anhydride (1.62 g, 6.68 mmol) was dissolved in absolute ethanol (100 mL) and the solution was refluxed. To this suspension under reflux, hydrazine hydrate (0.21 g, 0.21 mL, 6.68 mmol) was added dropwise and heating was maintained overnight. A brown colored precipitate appeared during reaction. After cooling, the precipitate was filtered off, washed several times with heptane and ether, and finally dried under vacuum (1.06 g, 62% yield). ¹H NMR (DMSO-d₆) δ (ppm): 5.84 (brs, 2H), 8.03 (s, 1H), 8.65-8.75 (m, 2H), 8.90 (s, 1H), 9.44 (s, 1H); ¹³C NMR (DMSO-d₆) δ (ppm): 122.1, 122.8, 123.6, 128.1, 129.2, 129.7, 130.7, 133.9, 136.4, 145.8, 159.3, 160.0; HRMS (ESI MS) m/z: theor: 257.0437 found: 257.0440 (M⁺ detected).

Synthesis of 2,5-diamino-1H-benzo[de]isoquinoline-1,3(2H)-dione (NDN2)



3-Amino-1,8-naphthalic acid anhydride (1.42 g, 6.68 mmol) was dissolved in absolute ethanol (100 mL) and the solution was refluxed. To this suspension, hydrazine hydrate (0.21 g, 0.21 mL, 6.68 mmol) was added dropwise and heating was maintained overnight. A yellow colored precipitate appeared. The reaction mixture was cooled to room temperature. The solid was filtered, washed several times with pentane and dried under vacuum (1.15 g, 76% yield). ^1H NMR (DMSO- d_6) δ (ppm): 5.93 (brs, 4H), 7.29 (d, 1H, $J = 1.4$ Hz), 7.62 (t, 1H, $J = 7.7$ Hz), 7.98 (d, 1H, $J = 1.7$ Hz), 8.04 (d, 1H, $J = 8.2$ Hz), 8.09 (d, 1H, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6) δ (ppm): 112.3, 119.6, 121.8, 122.2, 122.6, 126.0, 127.4, 132.2, 133.9, 148.4, 161.1, 161.3; HRMS (ESI MS) m/z : theor: 227.0695 found: 227.0698 (M^+ detected).

Synthesis of 2-amino-5,8-dinitro-1H-benzof[de]isoquinoline-1,3(2H)-dione (NDN3)



3,6-Dinitro-1,8-naphthalic acid anhydride (1.92 g, 6.68 mmol) was dissolved in absolute ethanol (100 mL) and the solution was heated until reflux. To this suspension, hydrazine hydrate (0.21 g, 0.21 mL, 6.68 mmol) was added dropwise and reflux was maintained overnight. During reaction, a beige colored precipitate appeared. The reaction mixture was cooled to room temperature and filtered. The precipitate was filtered off, washed several times with heptane and ether, and finally dried under vacuum (1.55 g, 77% yield). ^1H NMR (DMSO- d_6) δ (ppm): 5.80 (brs, 2H), 9.04 (d, 2H, $J = 1.8$ Hz), 9.74 (d, 2H, $J = 1.8$ Hz); ^{13}C NMR (DMSO- d_6) δ (ppm): 124.2, 125.8, 130.3, 130.6, 131.4, 147.1, 158.9; HRMS (ESI MS) m/z : theor: 302.0287 found: 302.0284 (M^+ detected).

Synthesis of 2,5,8-triamino-1H-benzo[de]isoquinoline-1,3(2H)-dione (NDN4)



3,6-Diamino-1,8-naphthalic acid anhydride (1.52 g, 6.68 mmol) was dissolved in absolute ethanol (100 mL) and the solution was refluxed. To this suspension, hydrazine hydrate (0.21 g, 0.21 mL) was added dropwise and the reaction was refluxed overnight. A yellow colored precipitate appeared. The reaction mixture was cooled to room temperature and filtered. The solution was concentration under vacuum. Addition of THF (5 mL) followed by pentane precipitated a light brown solid which was filtered off, washed several times with pentane and dried under vacuum (1.35 g, 84% yield). ¹H NMR (DMSO-d₆) δ (ppm): 5.70 (brs, 6H), 6.93 (d, 2H, J = 2.0 Hz), 7.59 (d, 2H, J = 2.0 Hz); ¹³C NMR (DMSO-d₆) δ (ppm): 109.7, 112.9, 117.0, 121.9, 135.5, 147.6, 160.9; HRMS (ESI MS) m/z: theor: 242.0804 found: 242.0807 (M⁺ detected).

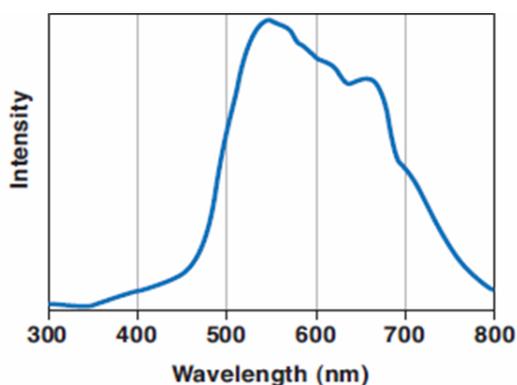


Figure S1. The emission spectrum of the halogen lamp.

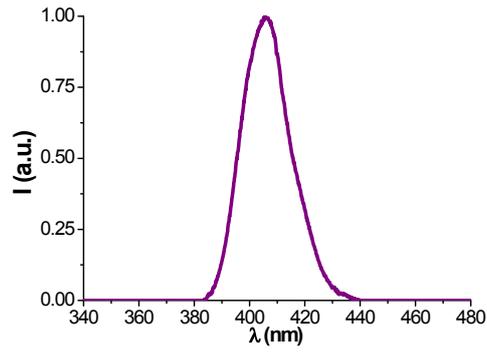


Figure S2. The emission spectrum of the LED centered at 405 nm*.

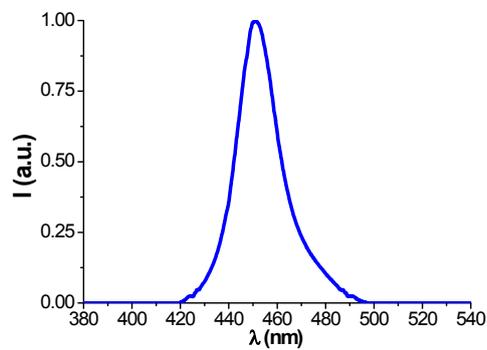


Figure S3. The emission spectrum of the blue LED centered at 455 nm*.

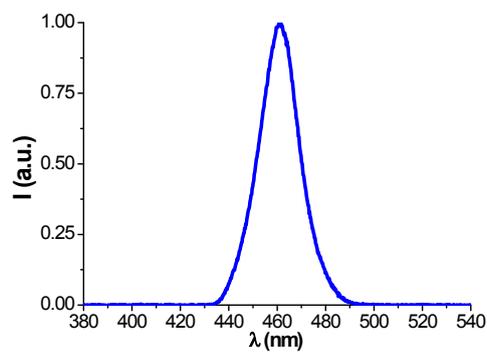


Figure S4. The emission spectrum of the blue LED centered at 470 nm*.

*For Figures S2-S4, 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/>)