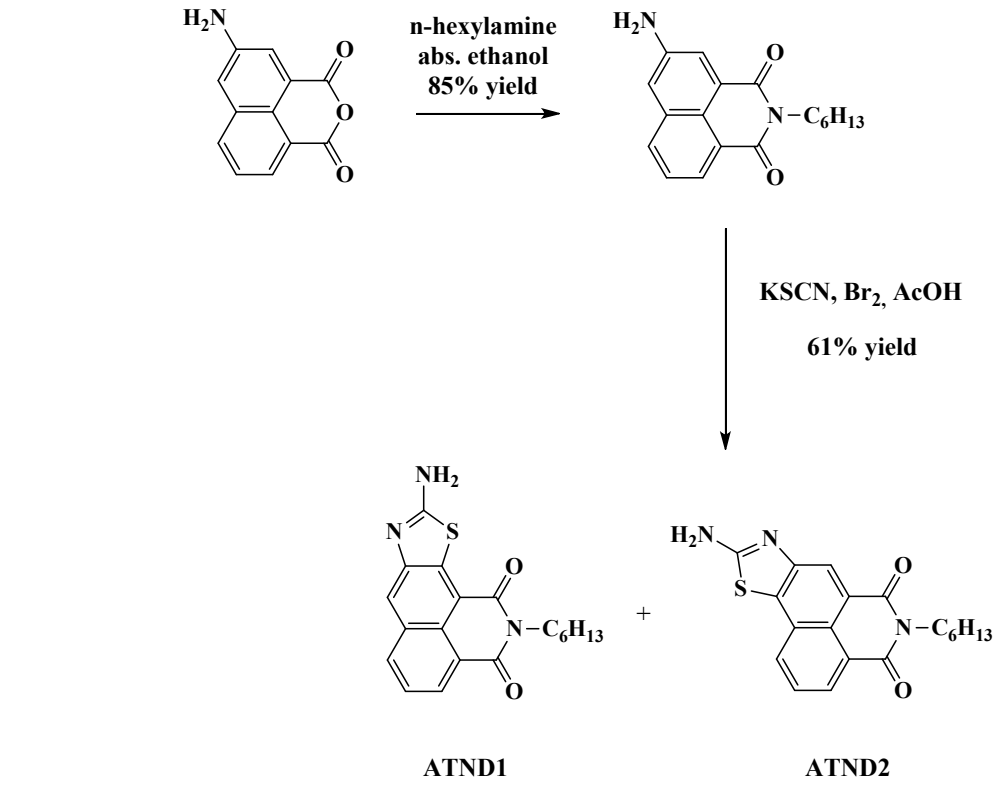
Supporting Information:

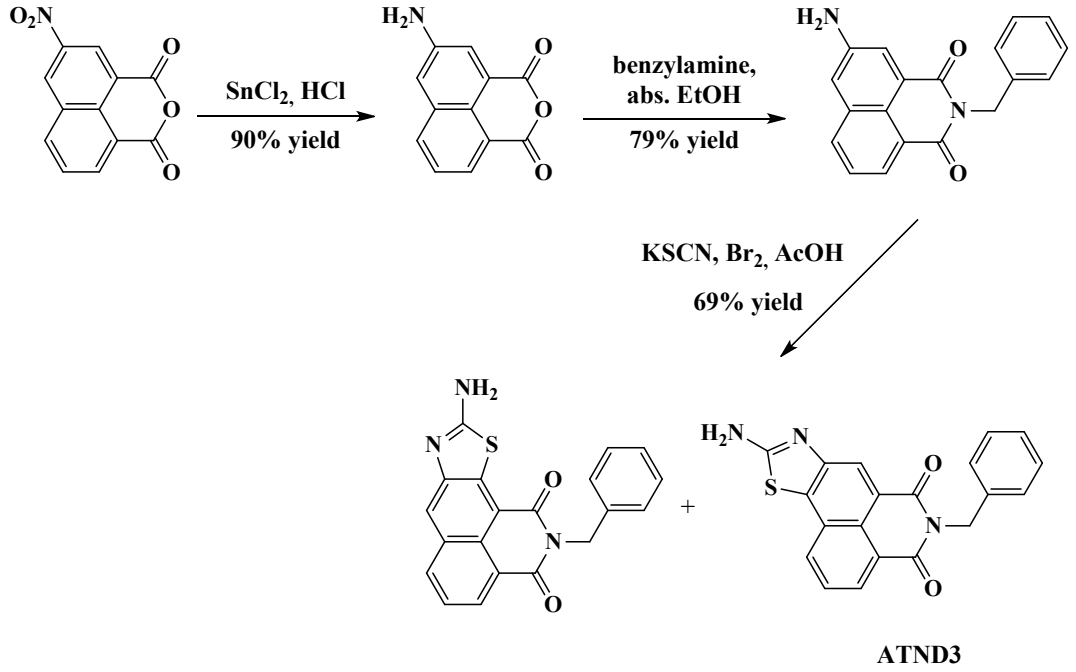
New Role of Aminothiazonaphthalimide Derivatives: Outstanding Photoinitiators for Cationic and Radical Photopolymerizations under Visible LEDs

Pu Xiao, Frédéric Dumur, Jing Zhang, Bernadette Graff, Jean Pierre Fouassier, Didier Gigmes and Jacques Lalevée

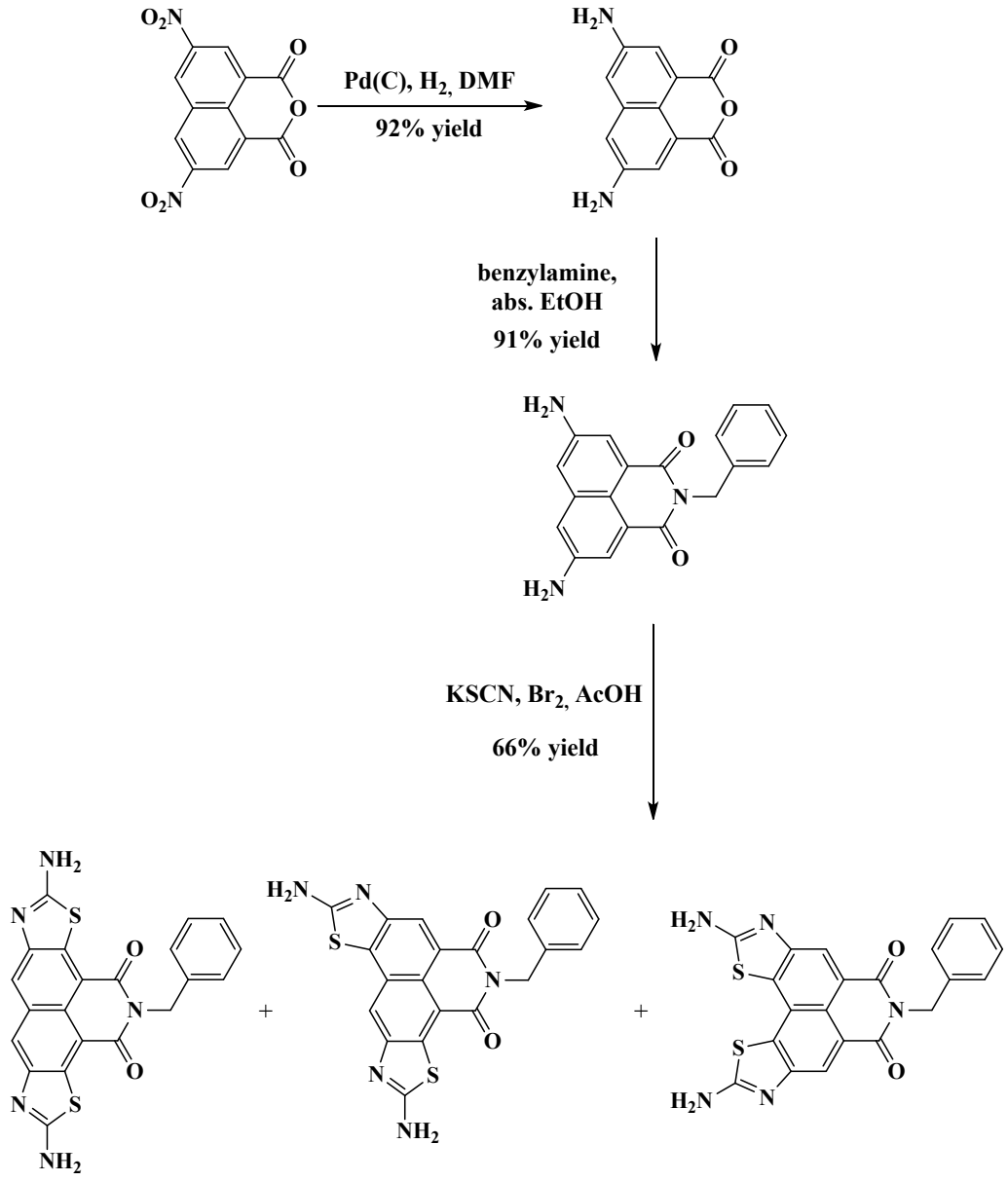
All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. 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. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm), acetone-d_6 (2.05 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm), acetone-d_6 (29.8 and 206.3 ppm). All the 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], 5-aminobenzo[*de*]isochromene-1,3-dione [J. Wang, L. Yang, C. Hou, H. Cao, Org. Biomol. Chem., 2012, 10, 6271], 5-amino-2-benzyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione [J. Zhang, F. Dumur, P. Xiao, B. Graff, D. Bardelang, D. Gigmes, J.-P. Fouassier, J. Lalevée, Macromolecules, 2015, 48, 2054], 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], 5,8-diamino-2-benzyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione [J. Zhang, F. Dumur, P. Xiao, B. Graff, D. Bardelang, D. Gigmes, J.-P. Fouassier, J. Lalevée, Macromolecules, 2015, 48, 2054] were synthesized as previously reported in the literature, without modifications and obtained in similar yields.



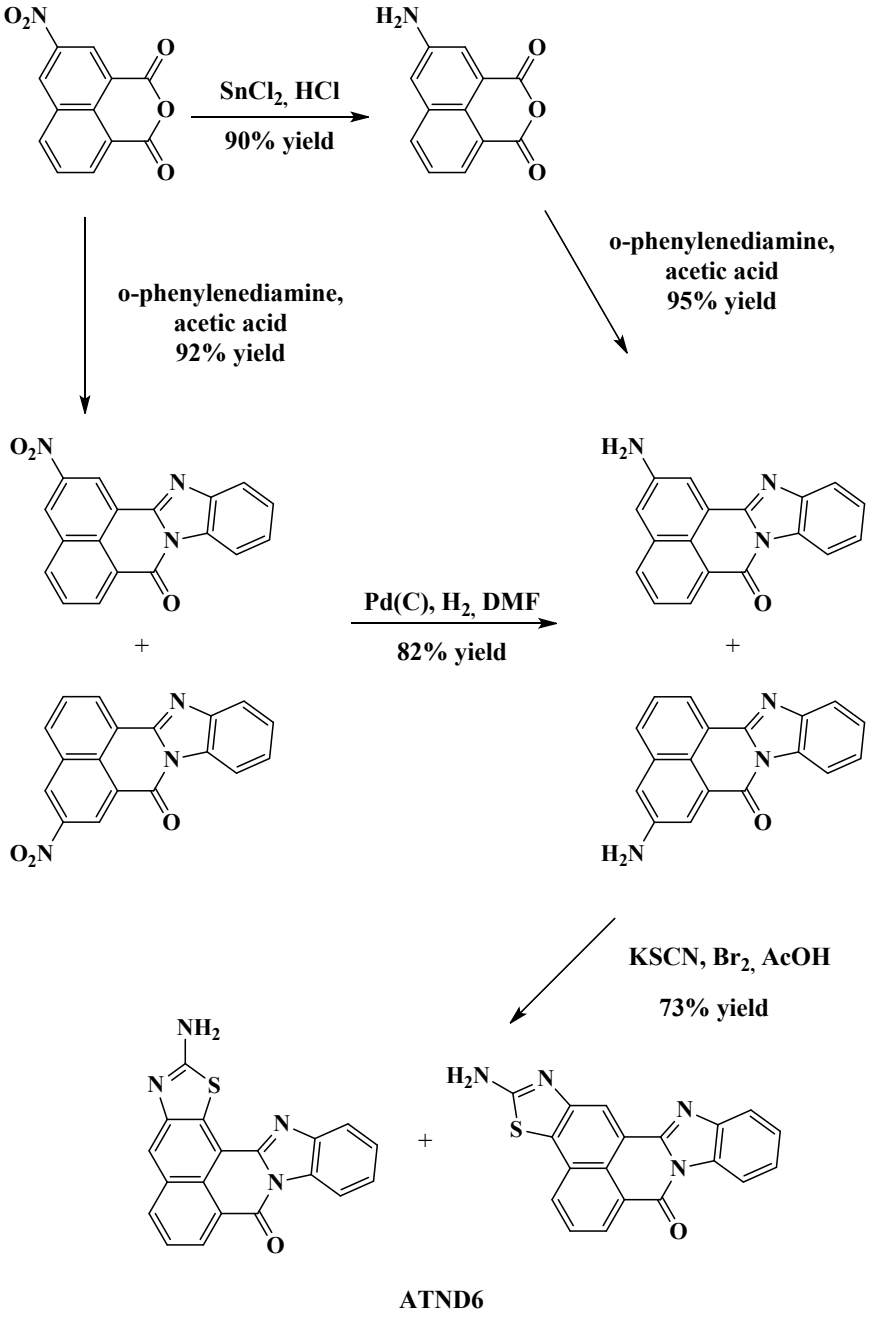
ATND1 ATND2



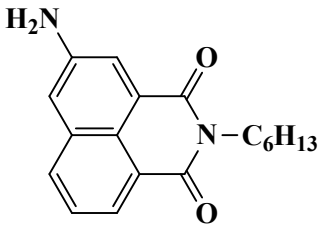
ATND3


Pd(C), H2, DMF
92% yield
benzylamine,
abs. EtOH
91% yield
KSCN, Br2, AcOH
66% yield

ATND5

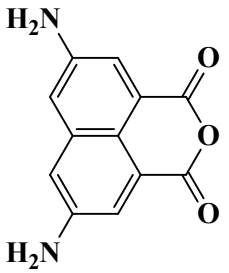


Synthesis of 5-amino-2-hexyl-1H-benzo[de]isoquinoline-1,3(2H)-dione



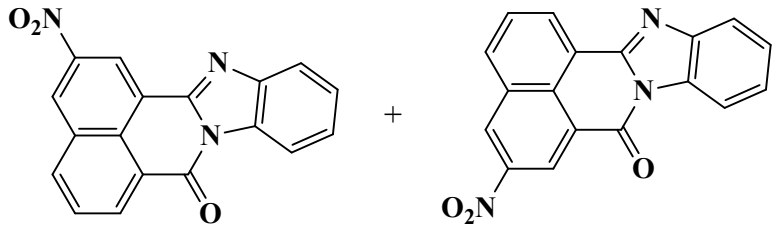
5-Aminobenzo[*de*]isochromene-1,3-dione (1.42 g, 6.68 mmol) and *n*-hexylamine (2.03 g, 2.65 mL, 20.04 mmol) was suspended in ethanol (50 mL) and the solution was refluxed overnight. After evaporation of the volatiles, the residue was purified by column chromatography (SiO_2) using dichloromethane as the eluent and the phthalimide was eluted in first fraction (1.68 g, 85% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.88 (t, 3H, J = 6.9 Hz), 1.31-1.43 (m, 6H), 1.67-1.75 (m, 2H), 4.14 (t, 2H, J = 7.6 Hz), 4.21 (brs, 2H, NH_2), 7.27 (d, 1H, J = 2.1 Hz), 7.58 (t, 1H, J = 7.5 Hz), 7.89 (d, 1H, J = 8.0 Hz), 8.02 (d, 1H, J = 2.3 Hz), 8.29 (dd, 1H, J = 7.2 Hz, J = 0.8 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 14.1, 22.6, 26.8, 28.1, 31.6, 40.5, 113.9, 122.0, 122.5, 123.6, 127.2, 127.3, 131.6, 133.4, 145.3, 164.2, 164.4; HRMS (ESI MS) *m*/*z*: theor: 297.1598 found: 297.1596 ($[M+H]^+$ detected).

Synthesis of 5,8-diaminobenzo[de]isochromene-1,3-dione



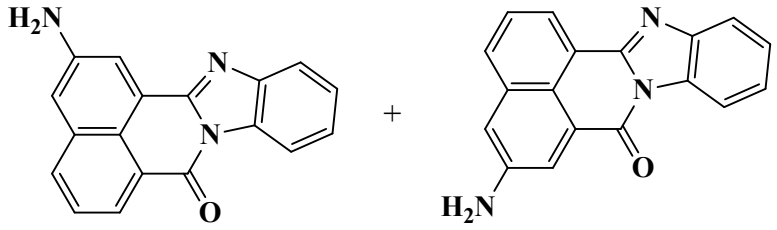
5,8-Dinitrobenzo[*de*]isochromene-1,3-dione (5.76 g, 20 mmol) was dissolved in DMF (40 mL) and 10% Pd/C (0.5 g) was added. The mixture was stirred under hydrogen at 40°C for 18 h. The catalyzer was then filtered off on a plug of celite 545, washed several times with ethanol. DMF was removed under reduced pressure. Addition of ether precipitated a red-brown solid which was washed several times with ether and dried under vacuum (4.19 g, 92% yield). Analyses were consistent with those previously reported [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, Bior. Med. Chem. 2011, 19, 6418]. ^{1}H NMR (DMSO-d_6) δ (ppm): 3.20-3.40 (brs, 4H), 7.00 (d, 2H, J = 2.0 Hz), 7.57 (d, 2H, J = 2.0 Hz); HRMS (ESI MS) *m*/*z*: theor: 229.0608 found: 229.0609 ($[M+H]^+$ detected); Anal. Calc. for $C_{12}H_8N_2O_3$: C, 63.2; H, 3.5; N, 12.3 Found: C, 63.3, H, 3.9; N, 12.4%.

Synthesis of 2-nitro-7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one and 5-nitro-7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one



3-Nitro-1,8-naphthalic acid anhydride (1.62 g, 6.68 mmol) and *o*-phenylenediamine (0.72 g, 6.68 mmol) was suspended in acetic acid (50 mL) and the solution was refluxed overnight. During reflux, a yellow precipitate formed. After cooling, the solvent was removed under reduced pressure. The residue was suspended in pentane, washed several times with pentane and dried under vacuum. The product was obtained under the form of a mixture of isomers. ^{1}H NMR (DMSO-d_6) δ (ppm): 7.52-7.55 (m, 4H), 7.90-7.93 (m, 2H), 8.07-8.15 (m, 2H), 8.42-8.45 (m, 2H), 8.71 (d, 1H, J = 8.3 Hz), 8.83-8.92 (m, 3H), 9.13 (d, 1H, J = 2.3 Hz), 9.19 (d, 1H, J = 2.2 Hz), 9.39 (d, 1H, J = 2.3 Hz), 9.54 (d, 1H, J = 2.2 Hz); HRMS (ESI MS) *m*/*z*: theor: 316.0717 found: 316.0719 ([M+H]$^+$ detected); Anal. Calc. for $C_{18}H_9N_3O_3$: C, 68.6; H, 2.9; N, 13.3 Found: C, 68.3, H, 2.9; N, 13.4%.

Synthesis of 2-amino-7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one



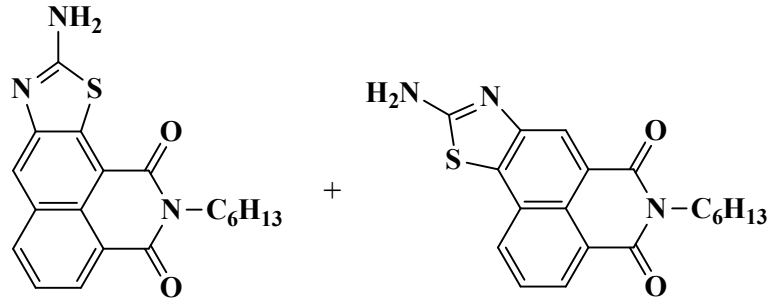
First procedure:

5-Aminobenzo[*de*]isochromene-1,3-dione (1.42 g, 6.68 mmol) and *o*-phenylenediamine (0.72 g, 6.68 mmol) was suspended in acetic acid (50 mL) and the solution was refluxed overnight. During reflux, a yellow precipitate formed. After cooling, the solvent was removed under reduced pressure. The residue was suspended in pentane, washed several times with pentane and dried under vacuum. The product was obtained under the form of a mixture of isomers (1.81 g, 95% yield).

Second procedure:

5-Nitrobenzo[*de*]isochromene-1,3-dione (1.5 g, 6.16 mmol) was dissolved in DMF (70 mL) and 10% Pd/C (0.5 g) was added. The mixture was stirred under hydrogen at 40°C for 18 h. The catalyzer was then filtered off on a plug of celite 545, washed several times with ethanol. The product was characterized by a low solubility so that the catalyzer was washed several times with boiling DMF. DMF was removed under reduced pressure. Addition of ether precipitated a solid which was washed several times with ether and dried under vacuum (1.44 g, 82% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.49-7.52 (m, 4H), 7.81-7.90 (m, 4H), 8.42-8.44 (m, 4H), 8.55-8.62 (m, 4H), 8.81 (s, 1H), 8.97 (s, 1H); HRMS (ESI MS) *m*/*z*: theor: 286.0975 found: 286.0977 ([M+H]$^{+}$ detected); Anal. Calc. for $C_{18}H_{11}N_3O$: C, 75.8; H, 3.9; N, 14.7 Found: C, 75.6, H, 3.7; N, 14.4%.

Synthesis of ***9-amino-2-hexyl-1H-benzo[de]thiazolo[4,5-h]isoquinoline-1,3(2H)-dione ATND1*** *and* ***9-amino-5-hexyl-4H-benzo[de]thiazolo[5,4-g]isoquinoline-4,6(5H)-dione ATND2***



ATND1 **ATND2**

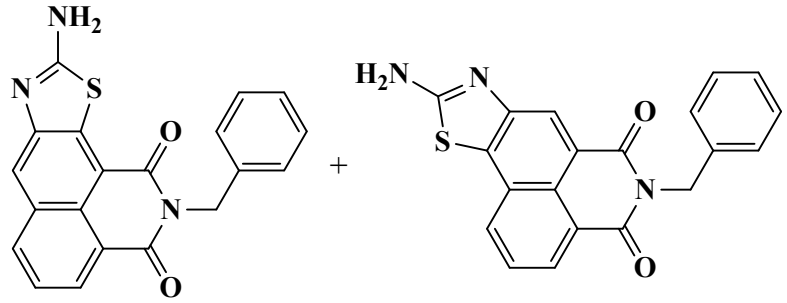
5-Amino-2-hexyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (1.39 g, 4.695 mmol) and KSCN (1.78 g, 19 mmol) were dissolved in 35 mL glacial acetic acid. A solution of Br_2 (0.76 g, 0.24 mL, 4.775 mmol) in glacial acetic acid (12 mL) was added dropwise, the mixture was stirred for 48 h, then filtered, and dried to get the yellow mixtures of the two isomers (1.07 g, 61% yield). Upon addition of pentane of ethanol to a solution of the two isomers in DCM, the two isomers could be separated from each other.

ATND1: ^{1}H NMR (DMSO-d_6) δ (ppm): 0.85 (t, 3H, J = 6.6 Hz), 1.20-1.38 (m, 6H), 1.59 (qt, 2H, J = 6.7 Hz), 3.98 (t, 2H, J = 7.5 Hz), 7.79 (t, 1H, J = 7.6 Hz), 8.23 (d, 1H, J = 8.2 Hz), 8.30 (d, 1H, J = 8.2 Hz), 8.31 (s, 1H); ^{13}C NMR (DMSO-d_6) δ (ppm): 13.9, 21.1, 21.9, 26.2,

27.3, 30.9, 120.5, 120.6, 122.7, 123.3, 125.6, 127.9, 128.4, 129.8, 131.0, 147.1, 163.0, 163.1, 168.1, 172.0; HRMS (ESI MS) *m*/*z*: theor: 354.1271 found: 354.1270 ($[M+H]^+$ detected).

ATND2: ^{1}H NMR (DMSO-d_6) δ (ppm): 0.84 (t, 3H, J = 6.6 Hz), 1.20-1.38 (m, 6H), 1.59 (qt, 2H, J = 6.7 Hz), 4.00 (t, 2H, J = 7.5 Hz), 7.79 (t, 1H, J = 7.6 Hz), 8.00 (brs, 1H, NH_2), 8.22 (d, 1H, J = 8.2 Hz), 8.30 (d, 1H, J = 8.2 Hz), 8.36 (s, 1H); ^{13}C NMR (DMSO-d_6) δ (ppm): 13.9, 21.9, 26.1, 27.4, 30.9, 119.9, 122.1, 122.7, 123.1, 125.8, 127.6, 128.0, 129.7, 130.1, 132.9, 150.9, 163.2, 163.4, 167.9; HRMS (ESI MS) *m*/*z*: theor: 354.1271 found: 354.1273 ($[M+H]^+$ detected).

Synthesis of 9-amino-5-benzyl-4H-benzo[de]thiazolo[5,4-g]isoquinoline-4,6(5H)-dione ***ATND3*** *and the mixture of 9-amino-2-benzyl-1H-benzo[de]thiazolo[4,5-h]isoquinoline-1,3(2H)-dione and 9-amino-5-benzyl-4H-benzo[de]thiazolo[5,4-g]isoquinoline-4,6(5H)-dione* ***ATND4***



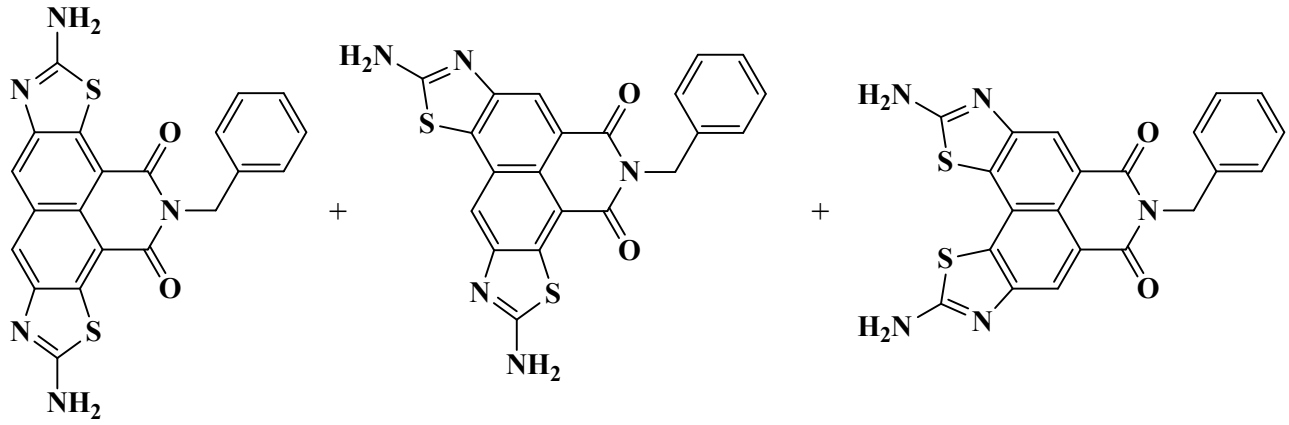
ATND3

5-Amino-2-benzyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (1.41 g, 4.695 mmol) and KSCN (1.78 g, 19 mmol) were dissolved in 35 mL glacial acetic acid. A solution of Br_2 (0.76 g, 0.24 mL, 4.775 mmol) in glacial acetic acid (12 mL) was added dropwise, the mixture was stirred for 48 h, then filtered, and dried to get the yellow mixtures of the two isomers (ratio: 38/62, 1.17 g, 69% yield). Upon precipitation with DCM/ethanol, a fraction of pure **ATDN3** could be separated from the mixture of isomers.

ATND4: ^{1}H NMR (DMSO-d_6) δ (ppm): 5.21 (s, 2H), 5.25 (s, 2H), 7.23-7.37 (m, 9H), 7.81-7.88 (m, 2H), 8.14-8.16 (m, 2H), 8.29 (d, 1H, J = 8.3 Hz), 8.37 (d, 1H, J = 8.3 Hz), 8.41-8.44 (m, 3H); ^{13}C NMR (DMSO-d_6) δ (ppm): 43.0, 98.2, 120.0, 121.9, 122.7, 122.8, 123.3, 125.6, 125.9, 126.8, 127.0, 127.5, 128.3, 128.5, 128.6, 129.1, 130.3, 131.5, 132.7, 134.1, 136.9, 137.1, 137.3, 145.6, 150.6, 162.6, 162.9, 163.3, 163.5, 166.6, 168.0, 171.6, 172.0; HRMS (ESI MS) *m*/*z*: theor: 360.0801 found: 360.0806 ($[M+H]^+$ detected).

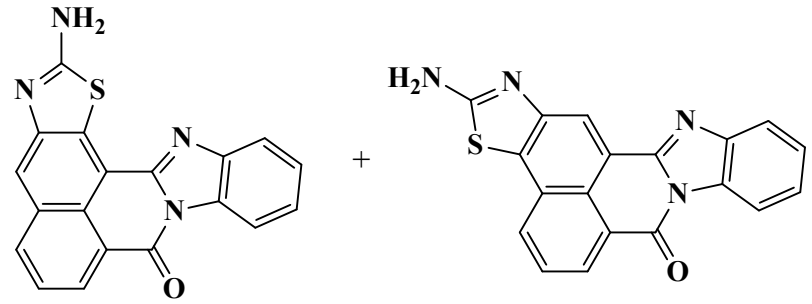
ATND3: ^{1}H NMR (DMSO-d_6) δ (ppm): 5.25 (s, 2H), 7.21-7.37 (m, 5H), 7.81 (t, 1H, J = 8.2 Hz), 8.07 (brs, 2H, NH_2), 8.26 (d, 1H, J = 8.3 Hz), 8.35 (d, 1H, J = 8.3 Hz), 8.40 (s, 1H); ^{13}C NMR (DMSO-d_6) δ (ppm): 21.0, 119.9, 122.2, 122.6, 123.2, 125.9, 127.0, 127.4, 127.5, 127.7, 128.3, 129.6, 130.3, 133.1, 137.4, 150.7, 163.4, 163.5, 167.9; HRMS (ESI MS) *m*/*z*: theor: 360.0801 found: 360.0805 ($[M+H]^+$ detected).

Synthesis of 5,10-diamino-2-benzyl-1H-thiazolo[4,5-h]thiazolo[4',5':5,6]benzo[1,2,3-de]isoquinoline-1,3(2H)-dione, 2,9-diamino-5-benzyl-4H-thiazolo[5,4-g]thiazolo[4',5':5,6]benzo[1,2,3-de]iso-quinoline-4,6(5H)-dione and 2,10-diamino-6-benzyl-5H-thiazolo[5,4-g]thiazolo[5',4':4,5]benzo [1,2,3-de]isoquinoline-5,7(6H)-dione ***ATND5***



5,8-Diamino-2-benzyl-*1H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (1.50 g, 4.695 mmol) and KSCN (3.56 g, 38 mmol) were dissolved in 35 mL glacial acetic acid. A solution of Br_2 (1.52 g, 0.48 mL, 9.55 mmol) in glacial acetic acid (12 mL) was added dropwise, the mixture was stirred for 48 h, then filtered, and dried to get the yellow mixtures of the two isomers (ratio 10/90, 1.34 g, 66% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 5.26 (s, 2H), 7.23-7.37 (m, 5H), 8.14 (brs, 2H, NH_2), 8.32 (s, 2H); ^{13}C NMR (DMSO-d_6) δ (ppm): 21.1, 119.1, 119.4, 120.3, 120.7, 127.0, 127.5, 128.3, 129.3, 137.4, 149.8, 163.3, 168.1, 172.0; HRMS (ESI MS) *m*/*z*: theor: 432.0583 found: 432.0588 ($[M+H]^+$ detected).

Synthesis of 2-amino-8H-benzo[de]benzo[4,5]imidazo[2,1-a]thiazolo[4,5-h]isoquinolin-8-one and 2-amino-7H-benzo[de]benzo[4,5]imidazo[2,1-a]thiazolo[5,4-g]isoquinolin-7-one ***ATND6***



2-Amino-7*H*-benzo[*de*]benzo[4,5]imidazo[2,1-*a*]isoquinolin-7-one (1.34 g, 4.695 mmol) and KSCN (1.78 g, 19 mmol) were dissolved in 35 mL glacial acetic acid. A solution of Br_2 (0.76 g, 0.24 mL, 4.775 mmol) in glacial acetic acid (12 mL) was added dropwise, the mixture was stirred for 48 h, then filtered, and dried to get the yellow mixtures of the two isomers (ratio 29/71, 1.17 g, 73% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.49-7.51 (m, 4H), 7.82-7.88 (m, 4H), 8.27 (d, 1H, J = 5.7 Hz), 8.41-8.45 (m, 3H), 8.55 (d, 1H, J = 6.2 Hz), 8.60 (d, 1H, J = 6.6 Hz), 8.62 (s, 1H), 8.81 (s, 1H), 8.84 (d, 1H, J = 8.2 Hz), 8.99 (d, 1H, J = 7.7 Hz), 10.7 (s, 1H), 10.7 (s, 1H); ^{13}C NMR (DMSO-d_6) δ (ppm): 115.2, 118.7, 119.6, 119.8, 120.6, 122.6, 123.1, 125.2, 125.5, 127.6, 129.5, 131.5, 132.7, 135.0, 138.1, 138.4, 143.3, 148.9, 160.3, 167.9, 169.2, 172.0.

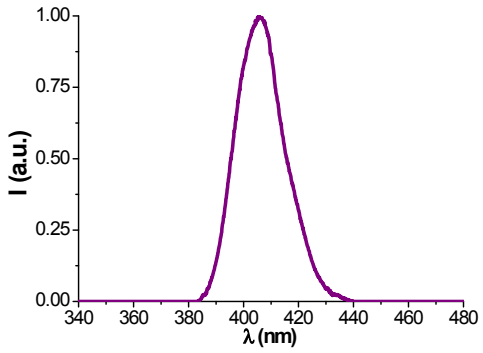


Figure S1. The emission spectrum of the LED centered at 405 nm*.

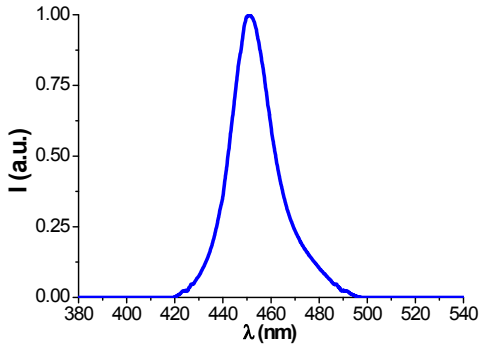


Figure S2. The emission spectrum of the blue LED centered at 455 nm*.

***For Figures S1 and S2, 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/)**

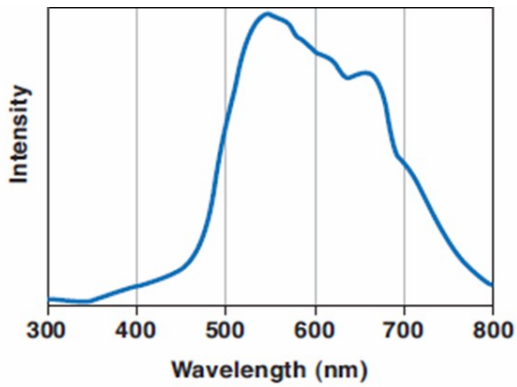


Figure S3. The emission spectrum of the halogen lamp.

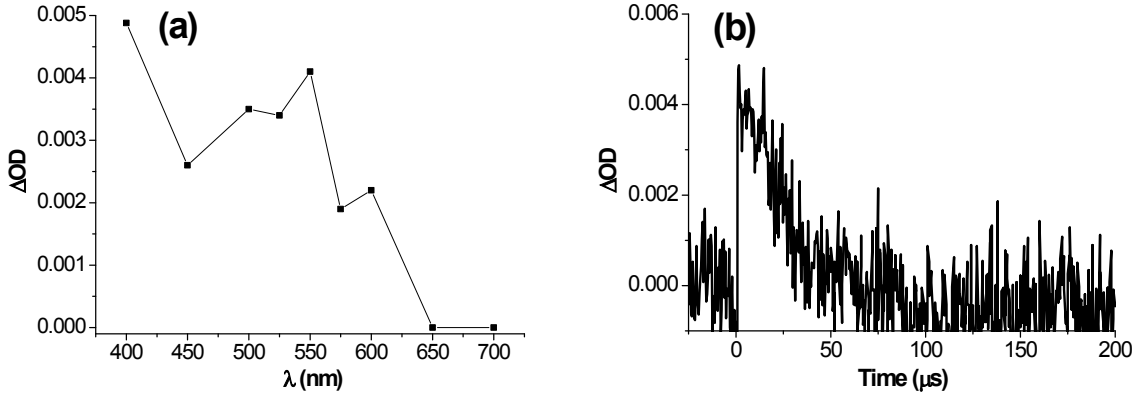


Figure S4. (a) Transient absorption spectrum recorded 5 μs after the laser excitation (at 355 nm) of ATND2 in nitrogen-saturated acetonitrile and (b) triplet state decay of ATND2 in nitrogen-saturated acetonitrile monitored at 550 nm (lifetime: 17.8 μs) immediately after the laser excitation at 355 nm.