Supporting Information to Accompany

Tunable Emissive Thin Films through ICT Photodisruption of Nitro-Substituted Triarylamines

Contribution from

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Table of content

Experimental Section

1. Synthetic procedures

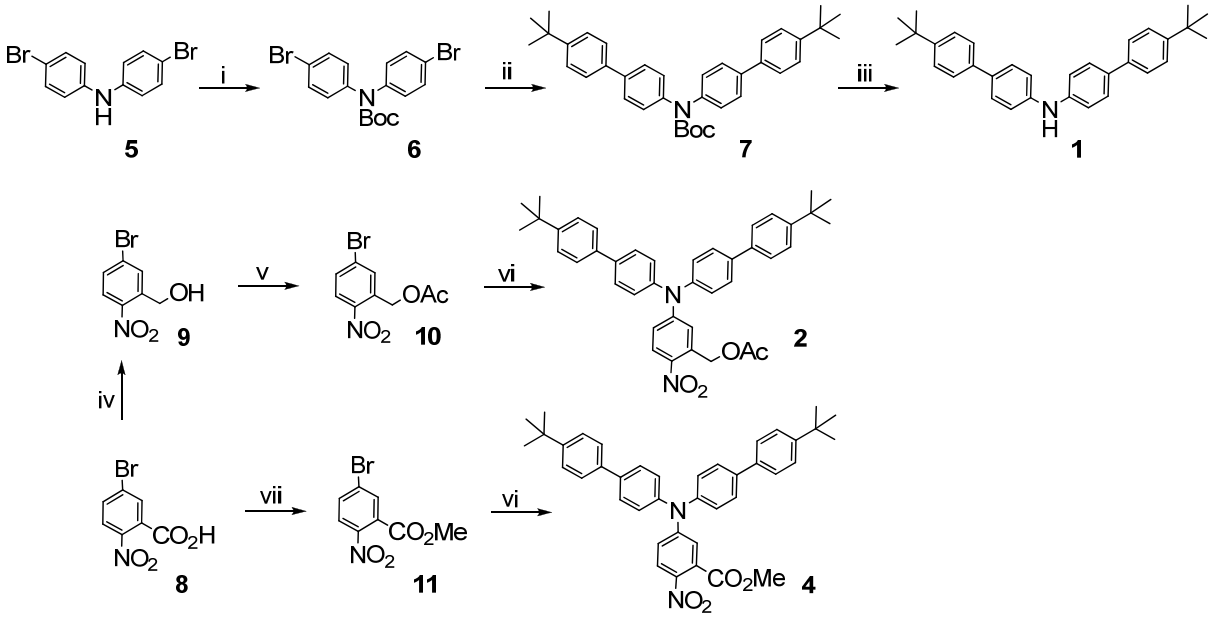
1.1. General

All chemical reagents and solvents were purchased from commercial sources (Aldrich, Acros, SDS) and used as received. Spectroscopic grade solvents purchased from Aldrich were used for photolysis experiments and spectroscopic measurements. All air-sensitive reactions were performed under argon using a vacuum line. Analytical TLC was performed on Kieselgel F-254 precoated plates. Visualization was done with UV lamp. Flash chromatography was carried out with silica gel 60 (230-400 mesh) from SDS. 4,4'-di(bromophenyl)amine **5**[1] and 4-[bis(4'-tert-butylbiphenyl-4-yl)amino]-2-nitrobenzene **3**[1] were synthesized according to literature procedures. Synthetic protocols were adapted to form 5-bromo-2-nitrobenzylic alcohol **9**[2] and 5-bromo-2-nitrobenzylethanoate **10**[3].

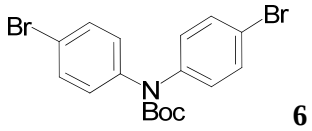
^{1}H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer, and chemical shifts δ were reported in ppm relative to TMS and referenced to the residual solvent. High resolution mass spectra

were obtained by MALDI-TOF (Voyager-DE sSTR, Perseptive Biosystems) or ESI-TOF (LCT, Waters) techniques.

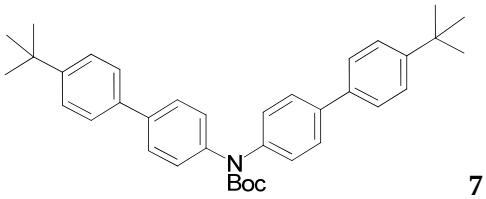
1.2. Synthesis



Scheme 1. i- Boc_2O, dimethylaminopyridine, THF rflx; ii- 4-*tert*-butylphenylboronic acid, $Pd(PPh_3)_4$, 2M Na_2CO_{3aq}, toluene, 80°C; iii- CF_3CO_2H, CH_2Cl_2, 0°C; iv- BH_3.THF 1M ; v- I_2, Ac_2O, RT; vi- $Pd(OAc)_2$, dppf, Cs_2CO_3, toluene, 80 °C; vii- $SOCl_2$, pyridine, methanol, 0°C.

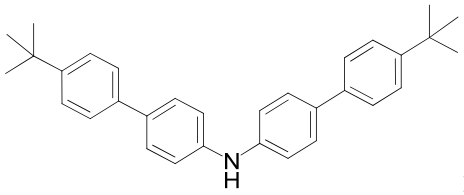


***Tert*-butyl bis(4-bromophenyl)carbamate 6.** A solution of bis(4-bromophenyl)amine **5** (4.25 g, 13.1 mmol), di-*tert*-butyl dicarbonate (3.14 g, 14.4 mmol), dimethylaminopyridine (0.32 g, 2.6 mmol) in dry tetrahydrofuran (10 mL) was heated at reflux for 4 hours. The solvent was removed under vacuum. The resulting solid was recrystallized in methanol to yield **6** as a fluffy white powder (5.04 g, 90 %). Mp 118°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.43 (d, ^3J(H,H) = 9 Hz, 4H), 7.06 (d, ^3J(H,H) = 8.7 Hz, 4H), 1.44 ppm (s, 9H; -O-*t*-Bu). ^{13}C NMR (100°MHz, $CDCl_3$, TMS): δ = 153.2, 141.8, 132.0, 128.6, 119.4, 82.1, 28.3. HRMS (MALDI-TOF), m/z (M^++Na): for $C_{17}H_{17}Br_2NO_2Na$ calculated 447.9524; found 447.9518. Elemental analysis: for $C_{17}H_{17}Br_2NO_2$ calculated C, 47.80, H, 4.01, N, 3.28; found C, 47.61, H, 3.97, N, 3.27.



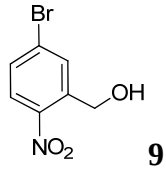
7

***Tert*-butyl-bis(4'-*tert*-butylbiphenyl-4-yl)carbamate 7.** A solution of *tert*-butyl bis(4-bromophenyl)carbamate **6** (4.0 g, 9.36 mmol) and tetrakistriphenylphosphinepalladium(0) (317 mg, 0.27 mmol) in toluene (70 mL) was stirred at room temperature under argon for 15 minutes. A solution of 4-*tert*-butylphenylboronic acid (3.66g, 20.5 mmol) in methanol (20 mL) was added, followed by the addition of a 2 $mol.L^{-1}$ sodium carbonate aqueous solution (18 mL). The resulting reaction mixture was heated at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was extracted with toluene. The combined layers were washed with brine and dried over anhydrous magnesium sulfate. Concentration under vacuum followed by silica gel column chromatography using an eluent gradient of petroleum ether: dichloromethane (final ratio 1:1) afforded **7** as a fluffy white solid (4.49 g, 90%). T_g 63°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ= 7.57 (d, ^3J(H,H)=8.7 Hz, 4H), 7.53 (d, ^3J(H,H)=8 Hz, 4H), 7.46 (d, ^3J(H,H)=8.7 Hz, 4H), 7.31 (d, ^3J(H,H)=8.7 Hz, 4H), 1.49 ppm (s, 9H; -O-*t*-Bu), 1.36 ppm (s, 18H; *t*-Bu). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ= 154.0, 150.4, 142.1, 138.5, 137.7, 127.4, 127.3, 126.8, 125.8, 81.5, 34.7, 31.5, 28.4 ppm. HRMS (MALDI-TOF), m/z (M^++Na): for $C_{37}H_{43}NO_2Na$ calculated 556.3191; found 556.3186.



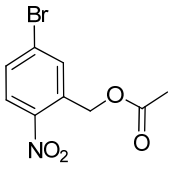
1

Bis(4'-*tert*-butylbiphenyl-4-yl)amine 1. A solution of **7** (1.86 g, 3.48 mmol) in freshly distilled dichloromethane (50 mL) was cooled at 0 °C. Trifluoroacetic acid (2.5 mL) was added dropwise over 15 min. The solution was stirred at 0 °C under argon for 30 minutes and 2 further hours at room temperature. The reaction mixture was neutralized with a saturated sodium hydrogenocarbonate aqueous solution. The organic layer was washed with water, dried over anhydrous magnesium sulfate and concentrated under vacuum. Compound **1** was obtained as a pure white solid (1.30 g, 85%). Mp 228 °C. ^{1}H NMR (400 MHz, d_6-acetone): δ =7.65 (s, 1H; NH), 7.57 (d, ^3J(H,H)=8.2 Hz, 4H), 7.54 (d, ^3J(H,H)=8.2 Hz, 4H), 7.46 (d, ^3J(H,H)=8,7 Hz, 4H), 7.24 (, ^3J(H,H)=8.5 Hz, 4H), 1.34 ppm (s, 18H; *t*-Bu). ^{13}C NMR (100°MHz, d_6-acetone): δ= 150.0, 143.7, 138.7, 133.5, 128.24, 126.6, 126.4, 118.4, 34.9, 31.6. HRMS (MALDI-TOF), m/z (M^+): for $C_{32}H_{35}N$ calculated 433.2770, found 433.2764.



9

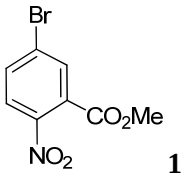
5-bromo-2-nitrobenzylic alcohol 9. To a mixture of concentrated sulphuric acid (10 mL) and nitric acid (68%) (20 mL) cooled to 0 °C, was added very slowly a solution of 3-bromobenzoic acid (6 g, 30 mmol) in concentrated sulphuric acid (10 mL). The reaction mixture was stirred at 0 °C during 6 hours. Water was added to precipitate a white solid which was filtered off, rinsed thoroughly with water and dried over P_2O_5 and used with no further purification. At this stage, two isomers 5-bromo-2-nitrobenzoic acid **8** and 3-bromo-2-nitrobenzoic acid were obtained in a ratio 88:12 in a total yield of 62 % (4.57 g). To a mixture of both acids (2 g, 7.7 mmol) in anhydrous THF (15 mL) was added a solution of BH_3.THF (23 mL, 23 mmol, 1M in THF) dropwise over 10-15 minutes at room temperature. The solution was stirred for a further two days and neutralized by careful addition of methanol. Afer evaporation to dryness, the isomers were separated by silica gel colum chromatography by using ethyl acetate:hexane 1:2 as an eluent. Two fractions containing respectively the targeted 5-bromo-2-nitrobenzylic alcohol **9** and its isomer 3-bromo-2-nitrobenzylic alcohol were obtained. Both products were recrystallized from a mixture of dichloromethane/petroleum ether to yield respectively **9** as a woolly cream product (610 mg, 37 %) and its ortho isomer as yellowish crystals. For **9** : Mp 96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.01 (d, ^3J(H,H)=8.8 Hz, 1H), 7.98 (d, ^4J(H,H)=2.2 Hz, 1H), 7.60 (dd, ^3J(H,H)=8.8 Hz, ^4J(H,H)=2.2 Hz, 1H), 5.02 (s, 2H, -CH_2O-), 2.40 (s, 1H, -OH). ^{13}C NMR (100°MHz, $CDCl_3$, TMS): δ = 139.1, 132.6, 131.6, 129.6, 126.6, 62.1. Elemental analysis: for $C_7H_6BrNO_3$ calculated C, 36.23, H, 2.61, N, 6.04; found C, 35.90.01, H, 2.58, N, 5.98.



10

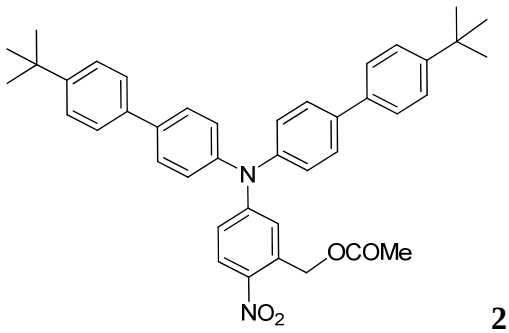
5-bromo-2-nitrobenzylethanoate 10. A solution of 5-bromo-2-nitrobenzoic acid **9** (567 mg, 2.44 mmol) and iodine (60 mg, 0.24 mmol) in acetic anhydride (5 mL) was stirred for 6 h 30. The solid was filtered off, dissolved in chloroform and washed with 5 mL of a saturated sodium thiosulfate aqueous solution. The organic layer was separated and washed twice with 20 mL of a saturated sodium hydrogenocarbonate aqueous solution and 20 mL of a saturated ammonium chloride aqueous solution. The organic layer was dried over anhydrous magnesium sulfate and evaporated under vacuum. Purification by silica gel column chromatography with chloroform as an eluent gave **10** as a beige powder (580 mg, 87%). Mp 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.01 (d, ^3J(H,H)=8.8 Hz, 1H), 7.75 (d, ^4J(H,H)=2.2 Hz, 1H), 7.63 (dd, ^3J(H,H)=8.3, ^4J(H,H)=2.2 Hz, 1H), 5.50 (s, 2H, -CH_2O-),

2.20 (s, 3H, -$COCH_3$). ^{13}C NMR (100°MHz, $CDCl_3$, TMS): δ = 170.2, 146.4, 134.5, 132.0, 129.1, 126.7, 62.4, 20.9. Elemental analysis: for $C_9H_8BrNO_4$ calculated C, 39.44, H, 2.94, N, 5.11; found C, 39.26, H, 2.92, N, 5.06.



11

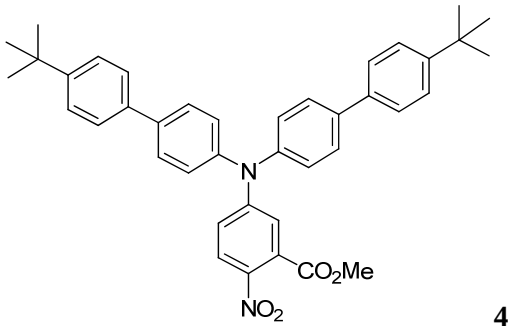
Methyl-5-bromo-2-nitrobenzoate 11. To a suspension of mixed acids 5-bromo-2-nitrobenzoic acid and 3-bromo-2-nitrobenzoic acid (1 g, 4.06 mmol) in pyridine (1.5 mL) at 0 °C were added dropwise thionyl chloride (0.4 mL) and then methanol (3.6 mL). The solution was stirred during 4 hours at 0 °C. Water was added to allow both the methyl 5-bromo-2-nitrobenzoate and methyl 5-bromo-2-nitrobenzoate to precipitate. After filtration, the compounds were purified by silica gel column chromatography with petroleum ether:ethyl acetate 9:1 as an eluent. The targeted isomer **11** was obtained as a cream white solid (620 mg, 58%). Mp 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.85 (d, ^4J(H,H)=2.0 Hz, 1H), 7.83 (d, ^3J(H,H)=8.7 Hz, 1H), 7.76 (dd, ^3J(H,H)=8.2 Hz, ^4J(H,H)=2.0 Hz, 1H), 3.94 ppm (s, 3H;-OMe). ^{13}C NMR (100°MHz, $CDCl_3$, TMS): δ = 164.7, 146.8, 13.8, 132.9 126.5, 127.9, 125.6, 53.7. Elemental analysis: for $C_8H_6BrNO_4$ calculated C, 36.95, H, 2.33, N, 5.39; found C, 37.18, H, 2.33, N, 5.19.



2

5-[bis(4'-tert-butylbiphenyl-4-yl)amino]-2-nitrobenzylethanoate 2. A solution of bis(4'-tert-butylbiphenyl-4-yl)amine **1** (396 mg, 0.91 mmol), arylbromide **10** (250 mg, 0.91 mmol), palladium (II) diacetate (10 mg, 0.045 mmol), 1,1′-bis(diphenylphosphino)ferrocene (dppf) (75 mg, 0.135 mmol), and cesium carbonate (438 mg, 1.35 mmol) in dry toluene (15 mL) was stirred overnight under argon at 80 °C. After filtration over a pad of Celite®, the filtrate was evaporated to dryness. The crude product was purified on silica gel chromatography column by using a mixture dichloromethane:petroleum ether as an eluent with an increase in gradient of polarity (composition 1:1 up to 7:3). Compound **2** was obtained as a bright orange product (450 mg, 79%). T_g 68 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.10 (d, ^3J(H,H)=9.2 Hz, 1H), 7.61 (d, ^3J(H,H)=8.7 Hz, 4H), 7.53 (d, ^3J(H,H)=8.7 Hz, 4H), 7.48 (d, ^3J(H,H=8.7 Hz, 4H), 7.27 (d, ^3J(H,H)=8.7 Hz, 4H), 6.99-6.96 (m, 2H), 5.50 (s, 2H, -CH_2O-), 1.91 (s, 3H, -$OCOCH_3$), 1.37 (s, 18H, *t*Bu). ^{13}C NMR (100°MHz, $CDCl_3$, TMS):

δ = 170.3, 152.8, 150.7, 144.3, 138.7, 137.2, 135.3, 128.4, 127.8, 126.8, 126.6, 126.0, 117.2, 116.9, 63.6, 34.7, 20.7. HRMS (MALDI-TOF), m/z (M+): for $C_{41}H_{42}N_2O_4$ calculated 626.3145, found 626.3139. UV-vis (cyclohexane), λ_{max} (ε_{max} ($mol^{-1}Lcm^{-1}$)): 399 (2.35×10^4), 321 (2.95×10^4) nm.



4

Methyl 5-[bis(4'-tert-butylbiphenyl-4-yl)amino]-2-nitrobenzoate 4. Palladium(II) diacetate (9 mg, 0.04 mmol), 1,1′-bis(diphenylphosphino)ferrocene (dppf) (66 mg, 0.12 mmol), bis(4'-tert-butylbiphenyl-4-yl)amine **1** (346 mg, 0.80 mmol) and cesium carbonate (390 mmol, 1.2 mmol) were successively added to a solution of arylbromide **11** (249 mg, 0.96 mmol) in dry toluene (10 mL) under argon. The reaction mixture was stirred overnight at 80 °C. After warming up to room temperature, the reaction mixture was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography with dichloromethane:petroleum ether as an eluent (initial and final compositions 1:1 and 7:3 respectively) afforded methyl 5-(bis(4'-tert-butylbiphenyl-4-yl)amino)-2-nitrobenzoate as a fluffy orange solid (500 mg, 95%). T_g 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.96 (d, ^3J(H,H)=9.5 Hz, 1H), 7.61 (d, ^3J(H,H)=8.7 Hz, 4H), 7.54(d, ^3J(H,H)=8.2 Hz, 4H), 7.48 (d, ^3J(H,H)=8.2 Hz, 3H), 7.26 (d, ^3J(H,H)=8.7 Hz, 4H), 7.05 (dd, ^3J(H,H)=9.5 Hz, ^4J(H,H)=2.7 Hz, 1H), 7.04 (d, ^4J(H,H)=2.7 Hz, 1H), 3.87 (s, 3H;-$COOCH_3$), 1.36 ppm (s, 18H;*t*-Bu). ^{13}C NMR (100°MHz, $CDCl_3$, TMS): δ= 167.4, 152.6, 150,7, 143.9, 139.0, 137.8, 137.1, 131.6, 129.1, 128.6, 128.3, 126.7, 126.6, 125.9, 119.1, 117.5, 53.4, 34.6, 31.4 ppm. HRMS (MALDI-TOF), m/z (M^+): for $C_{40}H_{40}N_2O_4$ calculated 612.2988, found 612.2982. UV-vis (cyclohexane), λ_{max} (ε_{max} ($mol^{-1}Lcm^{-1}$)): 399 (1.86×10^4), 317 (2.81×10^4) nm.

2. Ab-initio computations

TDDFT calculations were conducted using Becke's three-parameter hybrid functional and the correlation functional of Lee, Yang and Parr (B3LYP) with a 6-31G(d) basis set as implemented in the GAUSSIAN 03 package. Illustrations were obtained with GaussView 3.0.

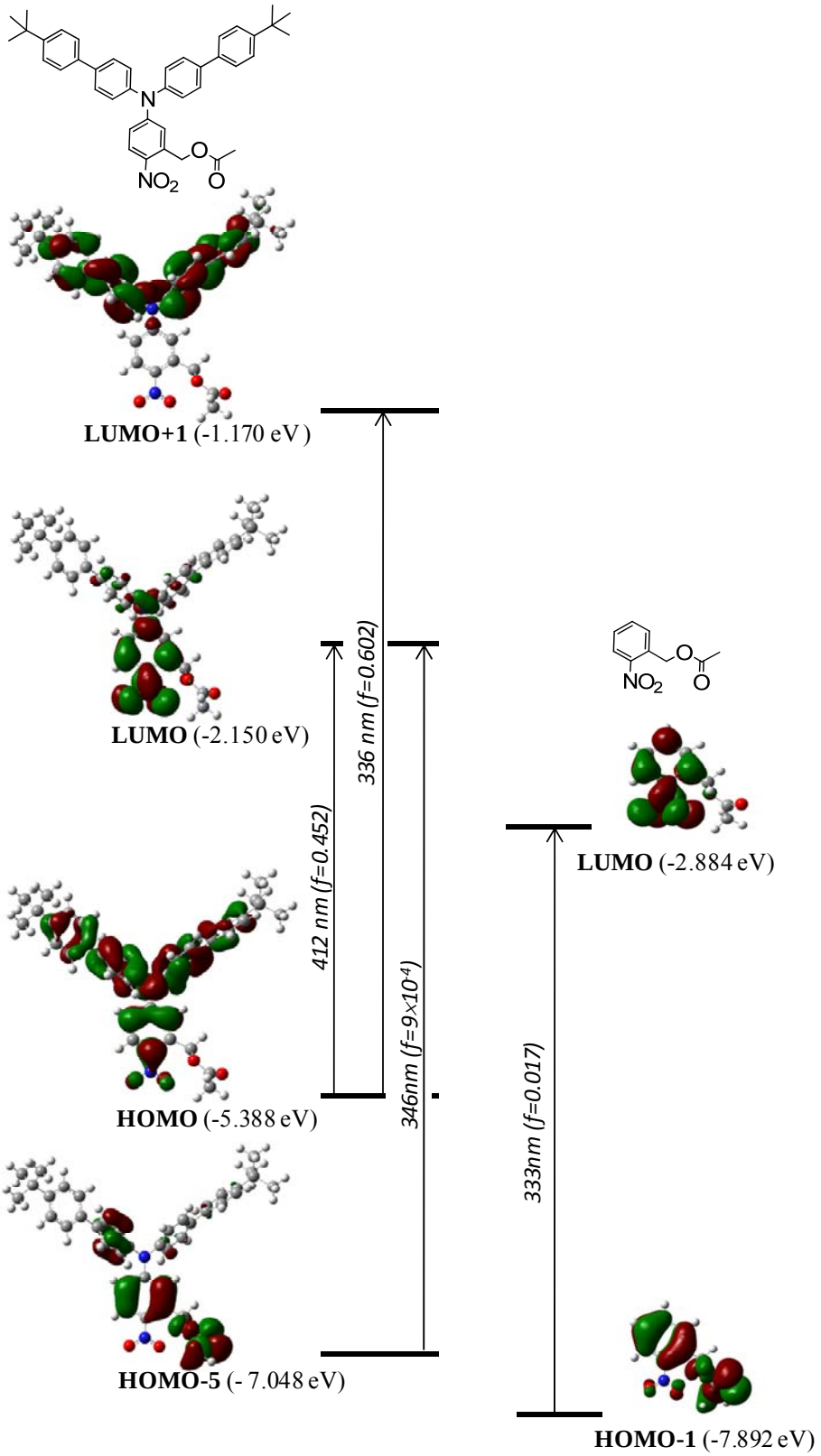


Figure S1. Computed energies and oscillator strengths of the UV-visible electronic transitions for compound **2** and the model 2-nitrobenzylethanoate. The molecular orbitals involved in the transitions are depicted through the spatial representation of their electronic density.

3. Photolysis experiments

Photolysis experiments were carried out on magnetically-stirred 2×10^{-5} molL^{-1} solutions of compounds **2**-**4** in cyclohexane by using a Hamamatsu Xe-Hg lamp source (LC8-06) equipped with a quartz optical fiber, and a 365 nm bandpass filter (Semrock) working at an intensity of 130 Mw. Absorption and fluorescence spectra were recorded by means of a Cary 500 spectrophotometer (Varian) and a Fluoromax 3 spectrofluorimeter (Jobin Yvon-Horiba) after each episode of UV illumination. Excitation was performed at 330 nm where evolution of the absorbance during the photocleavage reaction was minimal; excitation performed at much lower energy than photolysis provoked no additional chemical transformation. The percentage of photolysis was calculated from the emission or the absorption decrease at the CT band maximum. The one-photon photolysis quantum yields were determined by measuring the total incident intensity with a OPHIR powermeter.

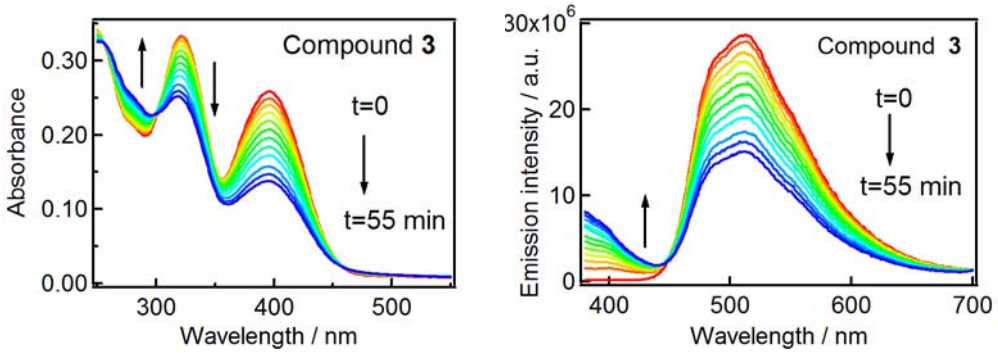


Figure S2. Evolution of the absorption (left) and emission (right) spectra of compound **3** in cyclohexane solution (2×10^{-5} molL^{-1}) under irradiation at 365 nm (260 mWcm^{-2}).

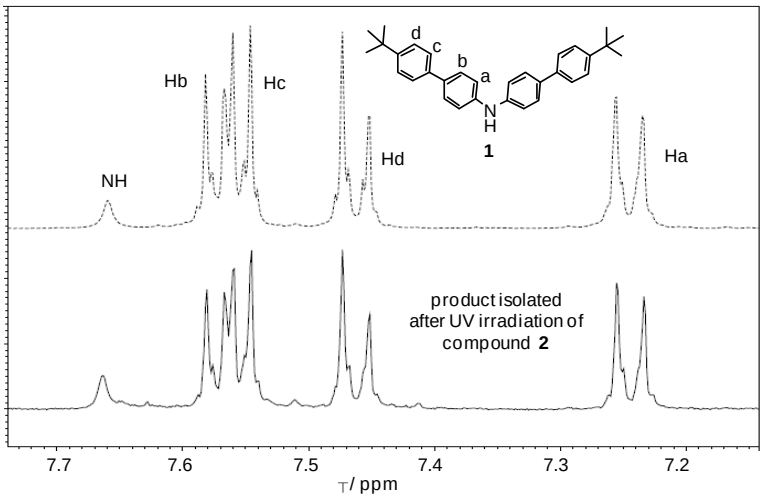


Figure S3. ^{1}H NMR spectra in cyclohexane-d_{12} (JEOL 400 MHz) of the major fraction isolated after silica gel column chromatography of a 10^{-3} mol.L^{-1} solution of **2** in cyclohexane irradiated at 365 nm (bold) and pure bis(4'-*tert*-butylbiphenyl-4-yl)amine **1** (dashed line).

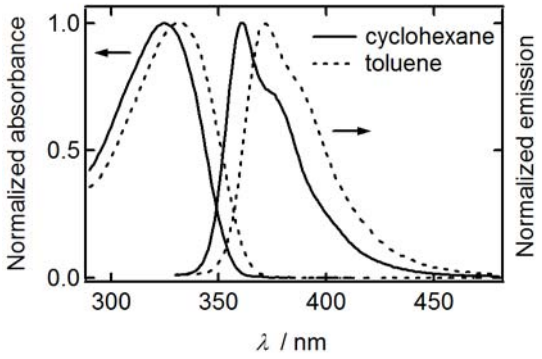


Figure S4. Normalized absorption and fluorescence (λ_{exc} = 320 nm) spectra of bis-(4'-*tert*-butylbiphenyl-4-yl)amine **1** in cyclohexane and toluene (4.6×10^{-6} mol.L^{-1}).

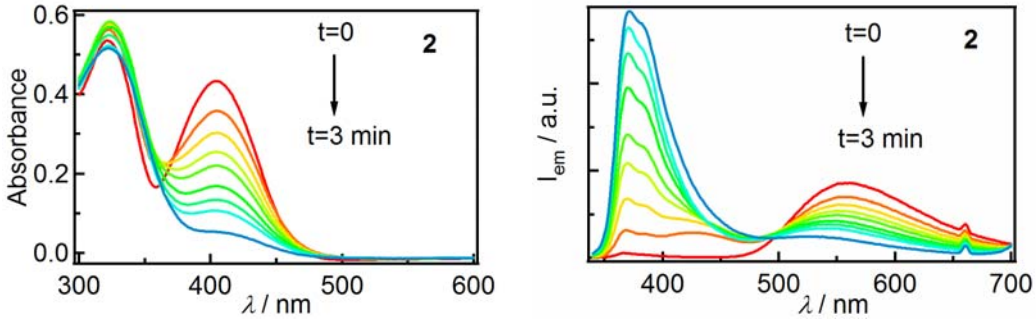


Figure S5. Evolution of the absorption (left) and emission (right) spectra of compound **2** in 1,4-cyclohexadiene solution (2×10^{-5} molL^{-1}) under irradiation at 365 nm (260 mWcm^{-2}).

4. Fluorescence imaging

Microscopic photolysis was done with a Leica SP2 inverted microscope (DMIRE2), using an oil immersion objective (magnifaction 63× NA 1.32) and an ultra-high pressure mercury lamp (bandpass centered at 360 nm) coupled to the objective through a liquid light guide. Epifluorescence imaging was performed by using a digital camera (Nikon DXM 1200). Alternatively, another excitation source and imaging setup were used, and involved a frequency-tripled Yb:KGW femtosecond laser (100 fs fwhm, 10 MHz, 343 nm, t-Pulse 200 Amplitude) which was directed to a Nikon 2000 TE inverted microscope in the wide-field configuration, reflected by an appropriate dichroic mirror and sent toward the sample through a high transmission microscope objective (Nikon S-Fluor, 40×, NA 0.90). Spectral analyses of the back-collected fluorescence were performed by means of a fiber-coupled spectrometer (Ocean Optics, Inc., ZD2000).

References

1. Ishow, E.; Brosseau, A.; Clavier, G.; Nakatani, K.; Pansu, R.; Vachon, J.-J.; Tauc, P.; Chauvat, D.; Mendonça, C. R.; Piovesan, E. *J. Am. Chem. Soc.* **2007**, *119*, 8970-8971.
2. Engler, T. A.; Henry, J. R.; Malhotra, S.; Cunningham, B; Furness, K.; Brozinick, J.; Burkholder, T. P; Clay, M. P.; Clayton, J.; Diefenbacher, C.; Hawkins, E.; Iversen, P. W.; Li, Y.; Lindstrom, T. D.; Marquart, A. L.; McLean, J.; Mendel, D.; Misener, E.; Briere, D.; O'Toole, J. C.; Porter, W. J.; Queener, S.; Reel, J. K.; Owens, R. A.; Brier, R. A.; Eessalu, T. E.; Wagner, J. R.; Campbell, R. M.; Vaughn R. *J. Med. Chem.* **2004**, *47*, 3934-3937.
3. Phukan P. *Tet. Lett.* **2004**, *45*, 4785-4787.