Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Diphenylamino-substituted Tristyryl vs. Triphenyl Isocyanurates: Improved Conjugation has Minimal Impact on Two-Photon Absorption

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1. Experimental Part.

General Procedures. All manipulations were carried out under an inert atmosphere of argon with dried and freshly distilled solvents (MeOH, distilled from Mg; THF, Et_2O and *n*-pentane, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2). Transmittance-FTIR spectra were recorded using a PerkinElmer Spectrum 100 spectrometer equipped with a universal ATR sampling accessory (400-4000 cm^{-1}). Raman spectra of the solid samples were obtained by diffuse scattering on the same apparatus and recorded in the 100-3300 cm^{-1} range (Stokes emission) with a laser excitation source at 1064 nm (25 mW) and a quartz separator with a FRA 106 detector. High-field NMR spectra experiments were performed on multinuclear Bruker 200 MHz or 400 MHz instruments (200DPX or Ascend400). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra. UV-Visible spectra were recorded using a Cary 5000 spectrometer or a Jasco V-570 (solutions) spectrophotometer. MS analyses were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (C.R.M.P.O., Université de Rennes 1) on a high resolution MS/MS ZABSpec TOF Micromass Spectrometer. Elemental analyses were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (C.R.M.P.O., Université de Rennes 1). The solid state structures (X-ray structural studies) were resolved at the "Centre de Diffractométrie X" (UMR CNRS 6226, Université de Rennes 1). The 4-bromocinnamic acid was synthesized from 4-bromobenzaldehyde (see ESI) and 4-ethynyl-*N,N*-diphenylaniline (**7**) was obtained as previously reported by some of us.[1]

Synthesis of 4-bromocinnamic acid. 4-Bromobenzaldehyde (5.00 g, 27.0 mmol) and malonic acid (6.20 g, 59.4 mmol) were dissolved in pyridine (100 mL). Piperidine (8 mL, 81.0 mmol) was then added. The mixture was heated to reflux for 12 h. After cooling to room temperature the solvents were evaporated. Water was added and the crude reaction mixture was extracted twice with Et_2O. The aqueous solution was then acidified with HCl 12N and the title compound was collected on a sintered funnel and

[1] G. Grelaud, M. P. Cifuentes, T. Schwich, G. Argouarch, S. Petrie, R. Stranger, F. Paul, M. G. Humphrey, *Eur. J. Inorg. Chem.* **2012**, 65–75.

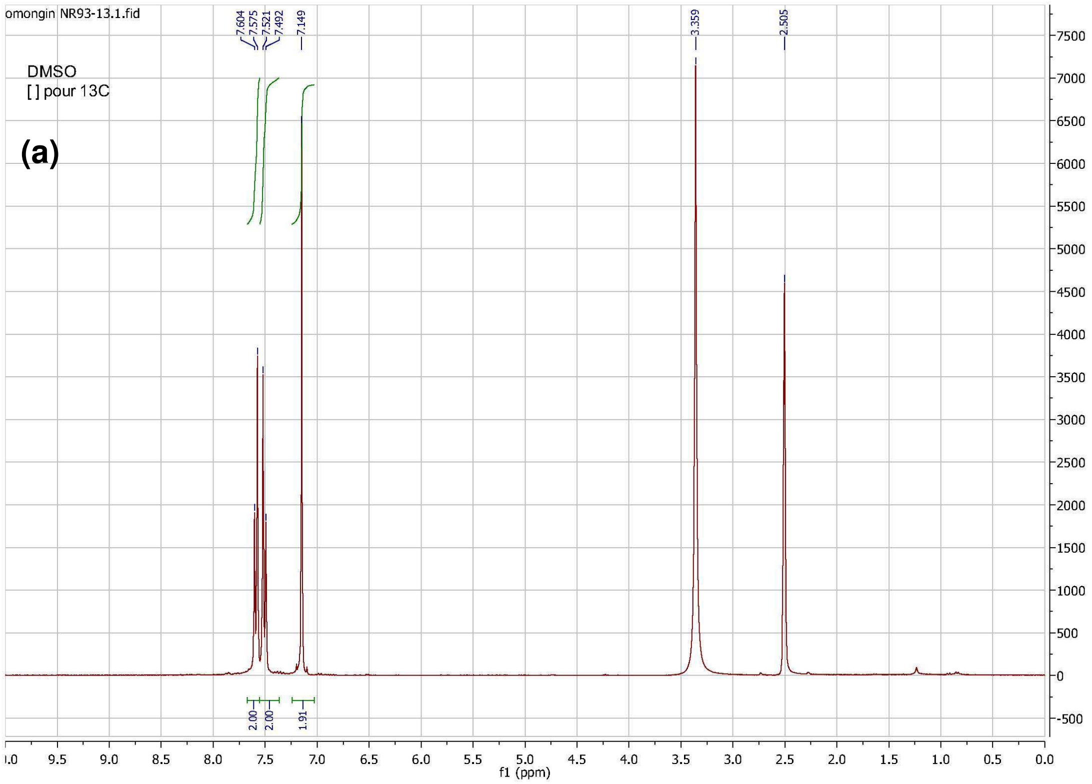
washed with dilute HCl. Yield: 82% (5.05 g). ^{1}H NMR (300 MHz, acetone-d_6) δ = 7.52 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 3.1 Hz, 4H), 6.44 (d, J = 16.0 Hz, 1H).[2]

Synthesis of 3-(4-bromophenyl)acryloyl azide (6-Br). A solution of 4-bromocinnamic acid in CH_2Cl_2 (80 mL) was cooled at 0 °C. Thionyl chloride (0.55 mL, 7.58 mmol) was then added dropwise. The ice bath was removed 10 min after completion of the addition and the reaction was continued by heating at 60 °C for 2 h. The reaction was monitored by ^{1}H NMR (a small fraction of the reaction medium was treated with methanol to form the corresponding ester and then the solvents were evaporated and the ^{1}H-NMR spectrum was examined in acetone-d_6). After completion of the reaction, the solvent was evaporated and the resultant acid chloride was solubilized in acetone (15 mL) and added dropwise to a cooled (ice bath) suspension of sodium azide (0.56 g). At the end of the addition, the reaction medium was brought to room temperature and left 12 h to complete the reaction (with TLC monitoring using CH_2Cl_2 as eluent). CH_2Cl_2 and a dilute aqueous solution of sodium bicarbonate were subsequently added to the reaction medium. After extraction with dichloromethane, the organic phase was dried and evaporated to give the title compound. Yield: 93% (1.17 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61 (d, J = 15.9 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 6.34 (d, J = 15.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 145.2, 132.7, 132.3, 129.9, 125.5, 119.7.[3]

The acid chloride intermediately formed was briefly characterized as its methyl ester by NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.55 (d, 1H, J = 16.0 Hz), 7.45 (d, 2H, J = 8.5 Hz), 7.31 (d, 2H, J = 8.5 Hz), 6.35 (d, 1H, J = 16.0 Hz), 3.74 (s, 3H).[4]

[2] W. Szymanski, B. Wu, B. Weiner, S. de Wildeman, B. L. Feringa, D. B. Janssen, *J. Org. Chem.* **2009**, *74*, 9152.
[3] T. Terai, M. Kohno, G. Boncompain, S. Sugiyama, N. Saito, R. Fujikake, T. Ueno, T. Komatsu, K. Hanaoka, T. Okabe, Y. Urano, F. Perez, T. Nagano, *J. Am. Chem. Soc.* **2015**, *137*, 10464–67.
[4] R. Brettle, A. J. Mosedale, *J. Chem. Soc. Perkin Trans. 1* **1988**, 2185-95.

2. $^{1}H/^{13}C\{^{1}H\}$ NMR Spectra of the Isocyanurates 3-NPh$_2$, 4-Br and of their Acryloyl Azide Precursor 6-Br



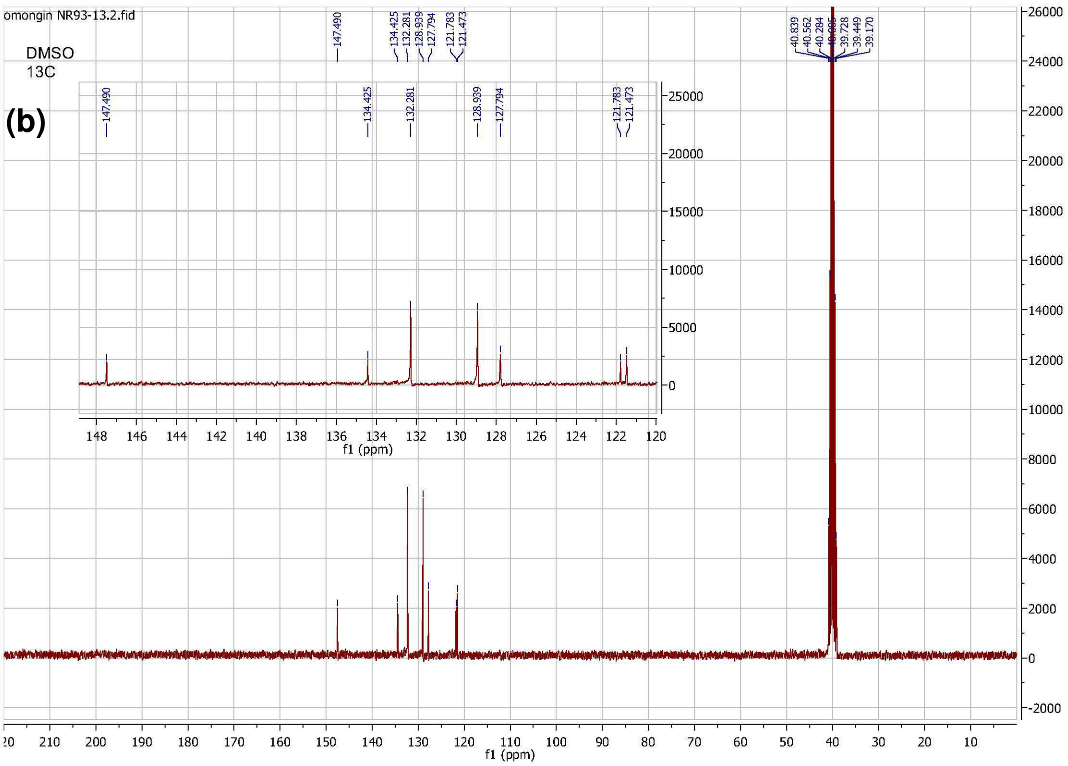


Figure S1. ^{1}H (a) and $^{13}C\{^{1}H\}$ (b) NMR Spectra at 300 and 75 MHz, respectively, for **4-Br** in DMSO-d_6.

(c)

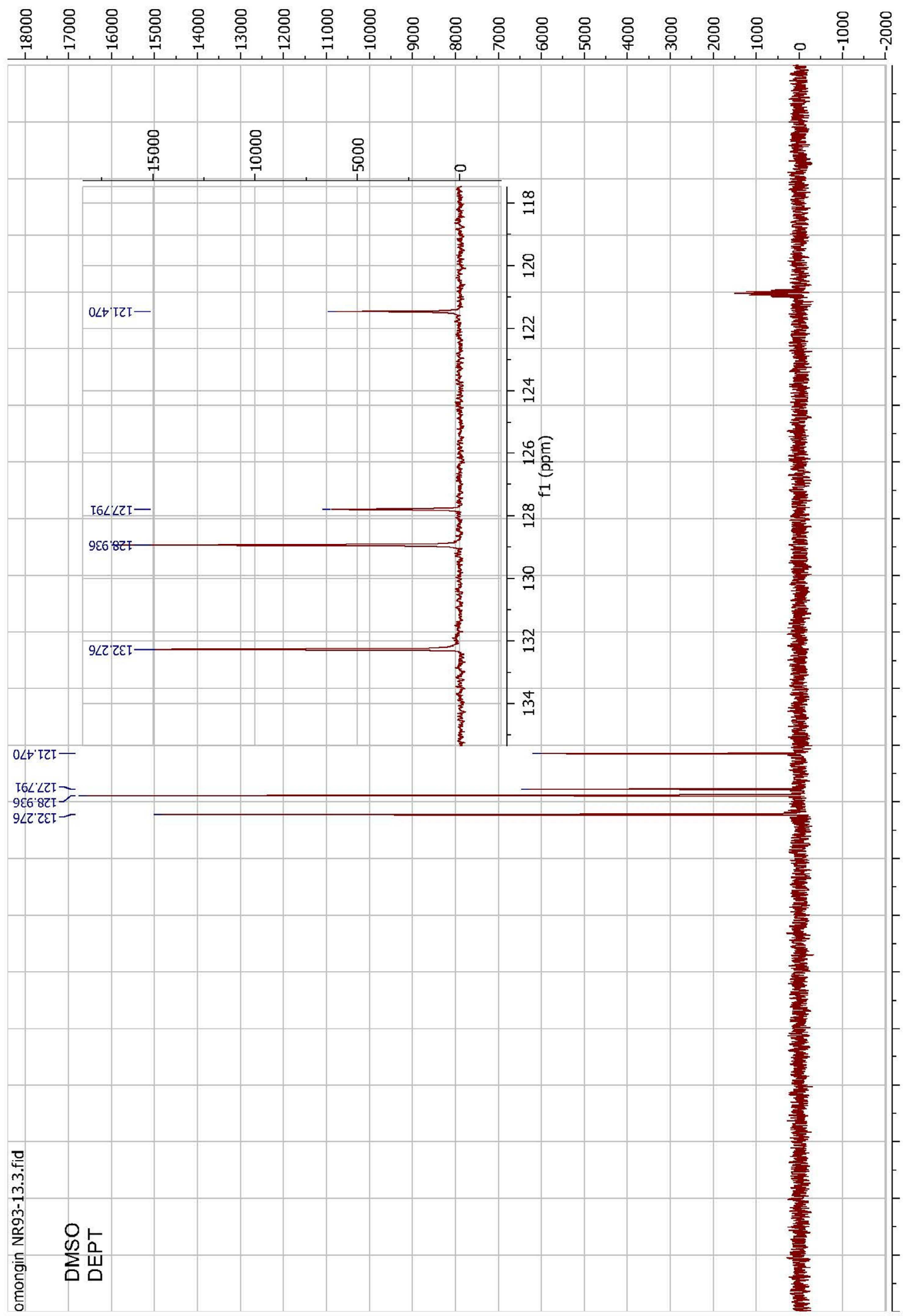
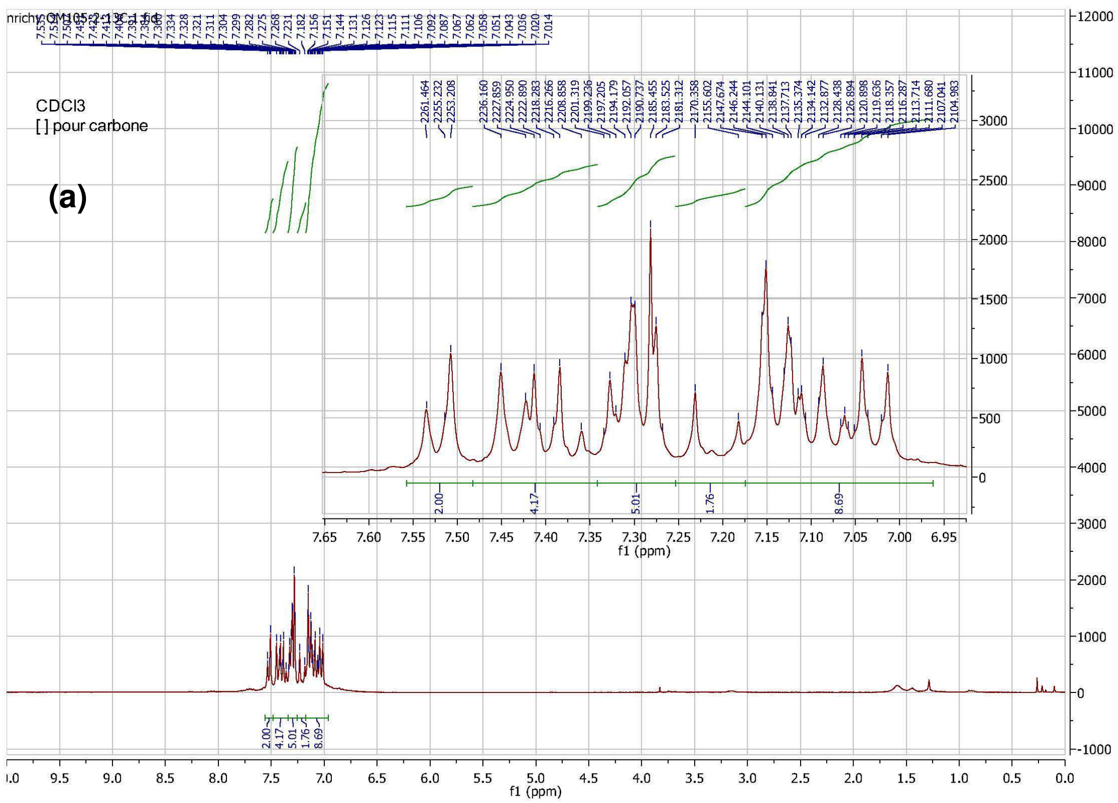


Figure S2. $^{13}C\{^{1}H\}$ NMR DEPT Spectrum (c) at 75 MHz for **4-Br** in DMSO-d_6.



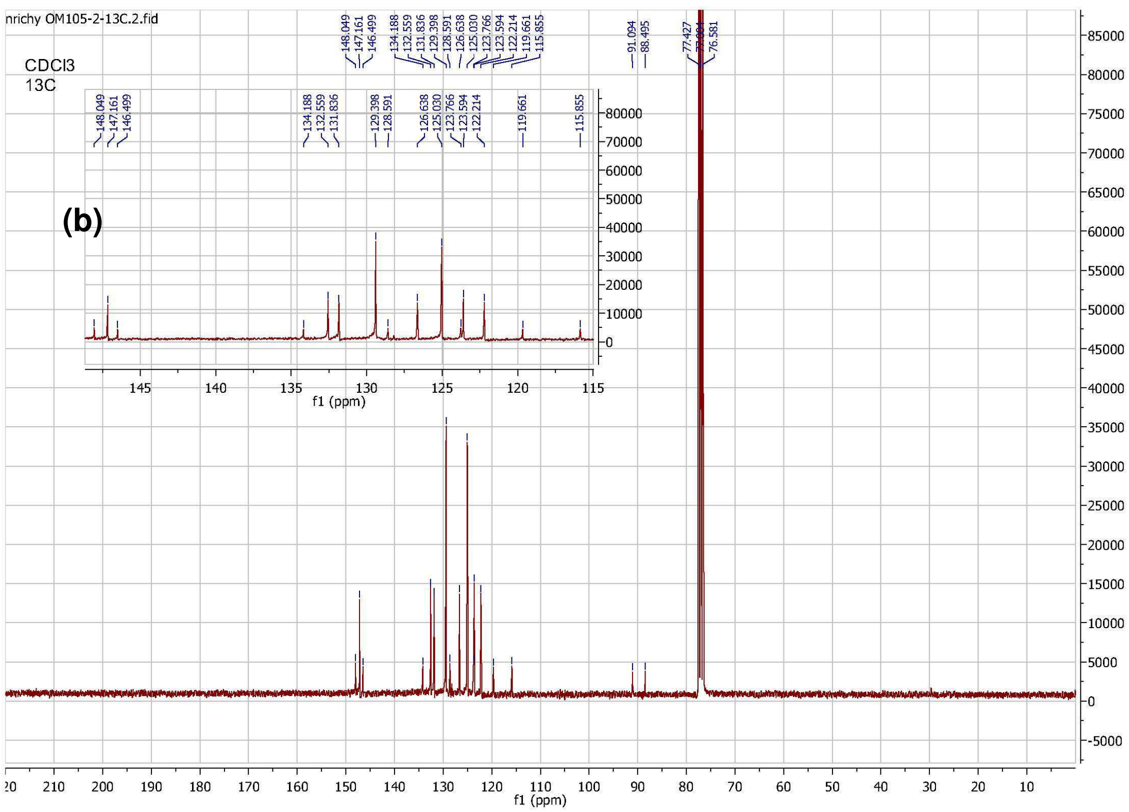
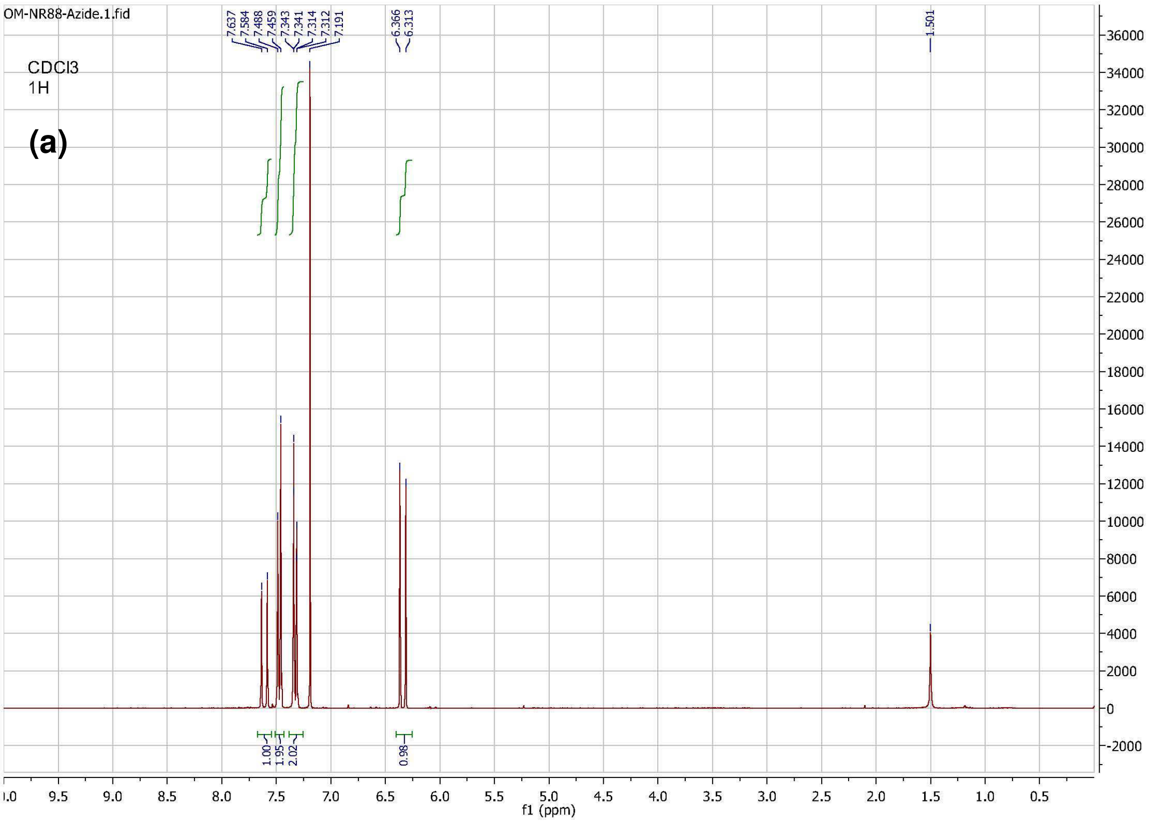


Figure S3. ^{1}H (a) and $^{13}C\{^{1}H\}$ (b) NMR Spectra at 300 and 75 MHz, respectively, for **3-NPh$_2$** in $CDCl_3$.



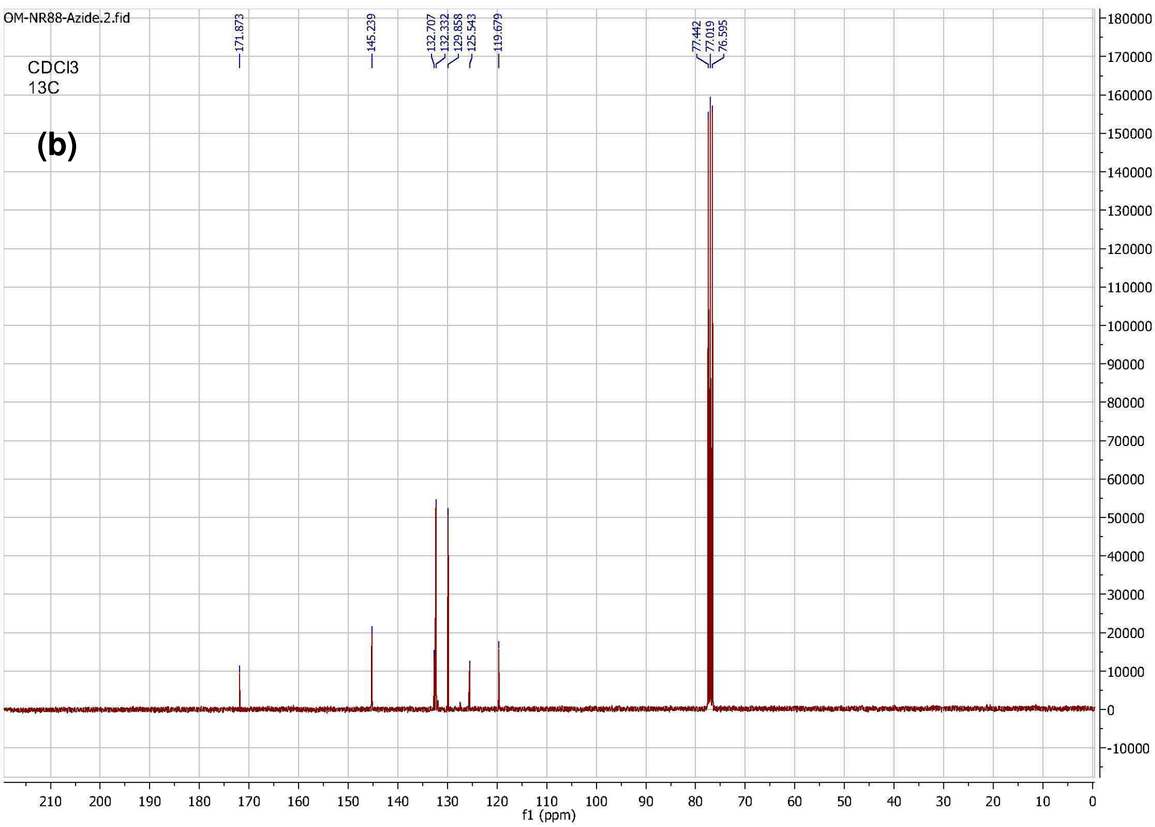


Figure S4. ^{1}H (a) and $^{13}C\{^{1}H\}$ (b) NMR Spectra at 300 and 75 MHz, respectively, for **6-Br** in $CDCl_3$.

3. Crystal Data, Data Collection and Refinement Parameters for 4-Br[5]

Cmpd	**4-Br**
formula	$C_{27}H_{18}Br_3N_3O_3$
Fw (g)	672.17
cryst. syst.	Monoclinic
space group	$P2_1/n$
a (Å)	19.931(3)
b (Å)	6.4376(9)
c (Å)	21.314(3)
α (deg)	90
β (deg)	100.969(5)
γ (deg)	90
V(Å^3)	2684.8(6)
Z	4
D(calcd) (g cm^{-3})	1.663
crystal size (mm)	0.58 × 0.07 × 0.04
F(000)	1320
abs. coeff. (mm^{-1})	4.514
N° total refl. / N° unique refl.	32585 / 6191
	[R(int) = 0.1077]
N° of variables/restraints/N° refl. > 2σ(I)	295/0/6191
final R	0.0978
Rw	0.1884
final R (all data)	0.1313
Rw (all data)	0.2002
Goodness of fit / F2 (Sw)	1.192

Table S1. Crystal Data, Data Collection, and Refinement Parameters for **4-Br**.

[5] See section 7 for more exhaustive listing of bond lengths (Å) and angles (°).

4. Absorption of 3-NPh$_2$ and 4-Br

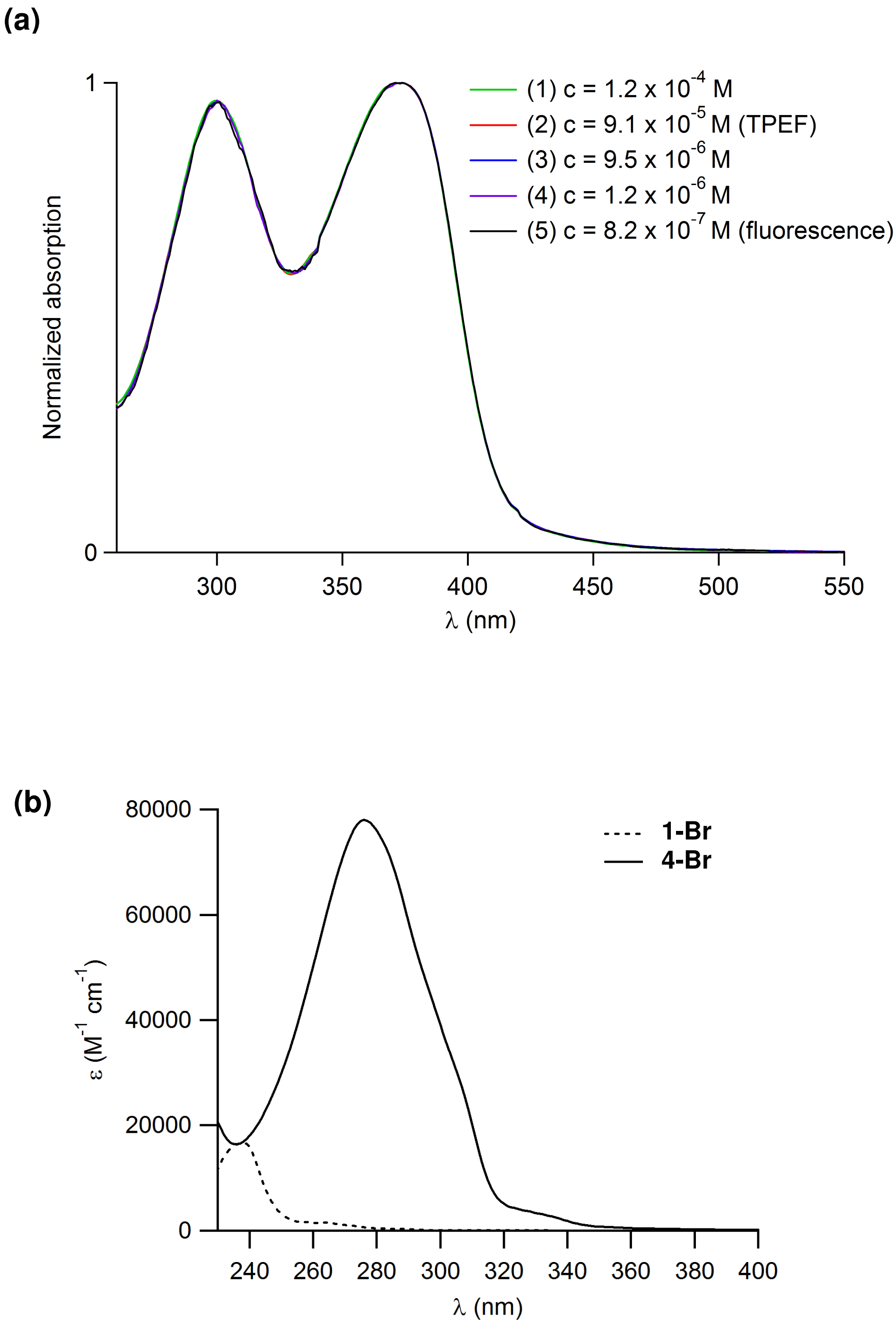


Figure S5. (a) Concentration dependence of the absorption spectrum of **3-NPh$_2$.** Normalized absorption spectra of **3-NPh$_2$** in dichloromethane: (1) and (2) measured in cuvettes with a 1 mm path length, (3), (4) and (5) in cuvettes with a 10 mm path length. (b) Absorption spectra of **4-Br** *vs.* **1-Br.**

5. Two-Photon Excited Fluorescence (TPEF) Data for 3-NPh_2

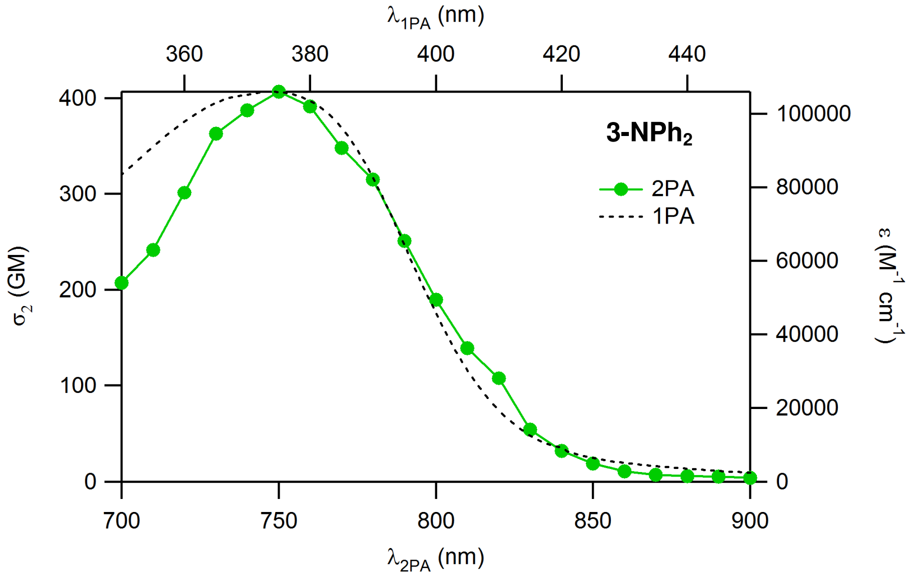


Figure S6. Overlay of one- and two-photon absorption spectra for **3-NPh_2** in CH_2Cl_2 (25 °C).

6. Cartesian Coordinates of the DFT Optimized Geometries at the MPW1PW91/6-31G* level in CH_2Cl_2 for 3-NPh_2, 4-NPh_2 and 4-Br

The supplementary file *molecules.xyz* contains the computed Cartesian coordinates (also given below) of all the molecules reported in this study in ".xyz" format for convenient visualization.

3-NPh_2, C_1 Symmetry

N	1.14970700	-0.74086400	0.01631500
C	1.24153200	0.65023700	-0.02797900
O	2.31760900	1.20379500	-0.10317200
N	0.03435700	1.33723200	0.02729500
C	-1.21705300	0.72198400	0.05477100
O	-2.23589000	1.37780400	0.09527500
N	-1.20731500	-0.66825000	0.02845400
C	-0.04837700	-1.44446100	0.06187500
O	-0.10618900	-2.65367400	0.12404500
C	2.40049400	-1.41929300	0.09325600
H	3.13002800	-0.86635700	0.67473200
C	-0.00001200	2.75882400	-0.06086000
H	-0.83802500	3.11323700	-0.65083200
C	-2.42477300	-1.40262000	0.13022700
H	-2.32999300	-2.27501200	0.76734100
C	0.87258800	3.57773200	0.53636900
H	1.65802800	3.16004100	1.16011500

C	-3.55389300	-1.08042500	-0.50978900
H	-3.56290100	-0.22594200	-1.18119700
C	2.67333000	-2.58562600	-0.50165100
H	1.91708200	-3.06184500	-1.11946500
C	3.94568300	-3.29791900	-0.39599900
C	4.15792800	-4.41012300	-1.22604800
C	4.97259800	-2.93303700	0.49205100
C	5.34578300	-5.12310600	-1.18968900
H	3.37228800	-4.71528400	-1.91511800
C	6.16224800	-3.63783200	0.53517300
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C	6.37250100	-4.74730200	-0.30681500
H	5.48909800	-5.98008500	-1.84318700
H	6.94454600	-3.34208200	1.22994800
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C	1.73417600	5.77325900	1.23914700
C	0.02473400	5.74335000	-0.45632900
C	1.76757000	7.15806600	1.19473900
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C	0.04983700	7.12556900	-0.50714700
H	-0.64935500	5.20761500	-1.12066600
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C	-5.05267900	-2.80422300	0.57167500
C	-7.07502900	-2.14820500	-1.22956300
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4-Br, C_1 Symmetry

C	3.75856500	-4.36213900	-0.74776800
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H	4.58364800	-6.19710200	-1.52033500
C	5.82875800	-5.30985800	0.00329000
C	6.01563300	-4.25759600	0.89085600
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C	5.05423900	-3.25520500	0.95253000
H	5.19492900	-2.42819000	1.64626400
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C	2.92687200	-2.21163100	0.28577700
H	3.24825700	-1.35363400	0.87006600
C	1.69850300	-2.23206000	-0.23965600
H	1.30062700	-3.08319300	-0.78160500
N	0.75074100	-1.17419200	-0.12432200
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O	2.30100100	0.47780300	-0.43571900
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H	3.31139300	4.41063600	1.65491100
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C	0.39063000	2.48558000	-0.24494700
H	-0.36956500	3.00905200	-0.81462900
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C	-1.23255800	0.77311300	-0.01101700
O	-2.07390100	1.64078200	0.08379500
C	-6.32928000	-0.34595900	-1.01177600
H	-6.06090200	0.40975000	-1.74793000
C	-7.65772300	-0.74065300	-0.90089900
H	-8.42232100	-0.30045500	-1.53933200
C	-7.99232300	-1.70527200	0.04114800
C	-7.02852600	-2.27214800	0.87080300
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C	-5.70699800	-1.86632600	0.74759500
H	-4.96586400	-2.30133200	1.41419600
C	-5.32921900	-0.90345900	-0.20196500
C	-3.94979400	-0.45124100	-0.39228800
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C	-2.87731900	-1.03655100	0.14965600
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O	-0.87398500	-2.76179300	0.02670800
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Br	2.82608000	9.08246600	-0.03603500
Br	-9.80114500	-2.25408400	0.21091400

4-NPh$_2$, C_1 Symmetry

N	1.11047709	-0.79374906	-0.08490001
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O	2.40131618	1.07007908	0.07881101
N	0.13212401	1.35385110	-0.05041900
C	-1.15865909	0.82082206	-0.10037701
O	-2.13232216	1.54130912	-0.11812001
N	-1.23901409	-0.56764304	-0.11676301
C	-0.12975401	-1.41751911	-0.16314101
O	-0.26276902	-2.61751320	-0.25995902
C	2.31671818	-1.54945912	-0.15860701
H	3.10092924	-1.00386407	-0.66433105
C	0.18607801	2.77257621	0.06962701
H	-0.67162205	3.16254324	0.59922404
C	-2.49894119	-1.22392109	-0.23308202
H	-2.42480019	-2.13396416	-0.81123306
C	1.14464409	3.55466027	-0.43980603
H	1.94541315	3.10717524	-1.01624308
C	-3.63874028	-0.80981306	0.33212303
H	-3.63258828	0.07861101	0.95209407
C	2.49748219	-2.76777221	0.36353503
H	1.69031913	-3.23441425	0.91557007
C	3.72855728	-3.54648427	0.25670002
C	3.88098730	-4.68559436	1.06081608
C	4.78536737	-3.22599825	-0.61143405
C	5.03592339	-5.45186644	1.03084208
H	3.08237524	-4.96445738	1.74216313
C	5.93668647	-3.99205931	-0.65983405
H	4.69855136	-2.38151818	-1.28734310
C	6.08728745	-5.11716439	0.16735301
H	5.12763339	-6.31519049	1.68012213
H	6.72729749	-3.73068729	-1.35420010
C	1.20470009	5.00605438	-0.28719902
C	2.11157416	5.73223143	-1.07315408
C	0.40308503	5.73379546	0.60785705
C	2.19898517	7.11390052	-0.99978808
H	2.74873121	5.20148840	-1.77468313
C	0.49197904	7.11162855	0.69925906
H	-0.28275502	5.21593140	1.27038109
C	1.38800711	7.82978860	-0.10947501
H	2.89821322	7.64491957	-1.63573213
H	-0.12641401	7.64391557	1.41326211

C	-4.93104238	-1.47513311	0.18757401
C	-5.98698048	-1.09104708	1.02714908
C	-5.19090940	-2.48817919	-0.75023406
C	-7.23026856	-1.70107213	0.96333407
H	-5.82209144	-0.30887902	1.76255513
C	-6.43216449	-3.09430524	-0.83187507
H	-4.42171334	-2.79055421	-1.45336311
C	-7.47511358	-2.71660121	0.02973900
H	-8.01852263	-1.39192311	1.64038612
H	-6.60817350	-3.86008630	-1.57895112
N	7.25909655	-5.89219144	0.11852101
N	1.47449411	9.22990169	-0.01636400
N	-8.73472265	-3.33530726	-0.05370600
C	0.31270502	10.00290879	0.22334002
C	0.34870003	11.06896985	1.12982709
C	-0.88291707	9.71706375	-0.44648003
C	-0.78920306	11.83576690	1.35394210
H	1.27082410	11.29119085	1.65588013
C	-2.02082815	10.47779679	-0.20227202
H	-0.91437307	8.89913670	-1.15816809
C	-1.98131915	11.54339790	0.69456905
H	-0.74489006	12.65888496	2.06009016
H	-2.94000823	10.24329576	-0.72974206
H	-2.86917622	12.13947193	0.87702807
C	2.72226221	9.88191574	-0.16990101
C	2.82073921	11.04541184	-0.94167007
C	3.86958630	9.37752373	0.45375903
C	4.04355131	11.69297090	-1.07868308
H	1.93592815	11.43713185	-1.43165511
C	5.09174039	10.02137575	0.29620302
H	3.79743229	8.48189563	1.06134508
C	5.18662439	11.18402484	-0.46596904
H	4.10333631	12.59424596	-1.68055113
H	5.97208043	9.61786672	0.78639206
H	6.14050945	11.68788292	-0.58051505
C	8.51563364	-5.27552040	-0.09510301
C	9.44630370	-5.85328146	-0.96660307
C	8.84694067	-4.08723231	0.56676704
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H	9.19265672	-6.77101049	-1.48608611
C	10.08140578	-3.48575227	0.34877103
H	8.13439361	-3.64057228	1.25179909
C	11.00959585	-4.06608831	-0.51324304
H	11.39608289	-5.71514345	-1.84326014
H	10.32304081	-2.56467320	0.86966107
H	11.97473990	-3.59793927	-0.67513905
C	7.19644852	-7.29654954	0.29093802
C	8.13195860	-7.95067962	1.10080009

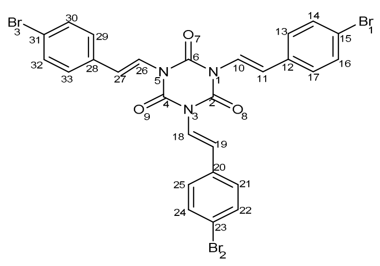
C	6.20588549	-8.04845464	-0.35174303
C	8.07866960	-9.33134370	1.25669409
H	8.89806570	-7.37192455	1.60534712
C	6.14902746	-9.42640473	-0.17540701
H	5.48433840	-7.54817655	-0.98862508
C	7.08582656	-10.07716675	0.62495605
H	8.81142367	-9.82374874	1.88813114
H	5.37498540	-9.99536775	-0.68062605
H	7.04285652	-11.15342686	0.75420706
C	-9.91585474	-2.58778920	0.17427201
C	-10.94911385	-3.12043924	0.95377007
C	-10.06895477	-1.31270610	-0.38288403
C	-12.11435792	-2.39141818	1.16384809
H	-10.83320282	-4.10573731	1.39217311
C	-11.22993388	-0.58336205	-0.15225201
H	-9.27582872	-0.89895807	-0.99630607
C	-12.26090292	-1.11809408	0.61768805
H	-12.90646297	-2.81845322	1.77074313
H	-11.33343788	0.40384403	-0.59136404
H	-13.16849599	-0.54914004	0.78931506
C	-8.83478166	-4.71409036	-0.35965703
C	-9.80654376	-5.16906739	-1.25864110
C	-7.97062859	-5.63984544	0.23707102
C	-9.91310376	-6.52503351	-1.54687712
H	-10.47488182	-4.45545134	-1.72820713
C	-8.07248664	-6.99176853	-0.07135301
H	-7.22260454	-5.29483939	0.94270807
C	-9.04535367	-7.44396658	-0.96042207
H	-10.67190483	-6.86176254	-2.24613117
H	-7.39495355	-7.69677656	0.39983603
H	-9.12677071	-8.50045663	-1.19296509

7. Comparison of Geometric Parameters for 4-Br Calculated at the MPW1PW91/6-31G* Level in CH_2Cl_2 and Experimental Data

Table S2. Comparison of geometric parameters for **4-Br** Calculated at the MPW1PW91/6-31G* Level in CH_2Cl_2 and Experimental Data.

Bond lengths (Å)			Bond angles (°)			Torsion angles (°)		
	Experimental geometry	Optimized geometry		Experimental geometry	Optimized geometry		Experimental geometry	Optimized geometry
N1-C2	1.40	1.39	N1-C2-N3	113.20	114.80	N1–C2- N3 –C4	-3.86	-5.30
C2-N3	1.40	1.39	C2-N3-C4	126.90	124.84	C2-N3-C4-N5	4.51	4.90
N3-C4	1.38	1.39	N3-C4-N5	114.72	115.74	N3-C4-N5-C6	-0.30	-0.11

C4-N5	1.39	1.39	C4-N5-C6	124.15	123.50	C4-N5-C6-N1	-3.90	-3.70
N5-C6	1.40	1.39	O7-C6-N1	122.01	121.74	O7-C6-N1-C2	-176.57	-177.40
C6-N1	1.39	1.39	O8-C2-N3	123.30	122.64	O8-C2-N3-C4	177.30	175.41
O7-N6	1.19	1.21	O9-C4-N5	124.16	123.13	O9-C4-N5-C6	-177.80	-175.41
O8-C2	1.20	1.21	C10-N1-C2	120.64	120.73	C10-N1-C2-N3	-178.37	-179.26
O9-C4	1.20	1.21	C11-C10-N1	131.16	124.62	C11-C10-N1-C2	-10.44	-41.11
C10-N1	1.45	1.42	C12-C11-C10	125.61	124.52	C12-C11-C10-N1	179.02	178.95
C11-C10	1.27	1.34	C13-C12-C11	119.30	123.51	C13-C12-C11-C10	22.33	11.84
C12-C11	1.50	1.46	C14-C13-C12	120.04	121.10	C14-C13-C12-C11	-178.03	-178.86
C13-C12	1.32	1.40	C15-C14-C13	116.64	119.15	C15-C14-C13-C12	-1.79	-0.41
C14-C13	1.37	1.38	C16-C15-C14	120.90	121.33	C16-C15-C14-C13	-0.22	-0.28
C15-C14	1.37	1.39	C17-C16-C15	121.54	118.77	C17-C16-C15-C14	-0.46	-0.32
C16-C15	1.37	1.39	Br1-C15-C14	120.17	119.27	Br1-C15-C14-C13	-179.55	-179.85
C17-C16	1.42	1.39	C18-N3-C4	112.71	114.48	C18-N3-C4-N5	-179.02	-174.50
C17-C12	1.39	1.40	C19-C18-N3	122.97	124.37	C19-C18-N3-C2	-45.27	-42.62
Br1-C15	1.90	1.90	C20-C19-C18	122.14	124.87	C20-C19-C18-N3	-172.60	-174.50
C18-N3	1.47	1.42	C21-C20-C19	116.54	118.26	C21-C20-C19-C18	171.20	171.06
C19-C18	1.27	1.33	C22-C21-C20	120.67	121.51	C22-C21-C20-C19	-173.92	-179.10
C20-C19	1.52	1.46	C23-C22-C21	120.80	118.77	C23-C22-C21-C20	-0.47	-0.25
C21-C20	1.38	1.40	C24-C23-C22	120.90	121.32	C24-C23-C22-C21	-1.08	-0.22
C22-C21	1.36	1.40	C25-C24-C23	117.03	119.16	C25-C24-C23-C22	0.62	0.18
C23-C22	1.36	1.39	Br2-C23-C22	119.70	119.41	Br2-C23-C22-C21	177.43	179.84
C24-C23	1.40	1.40	C26-N5-C6	114.70	115.11	C26-N5-C6-N1	179.11	176.77
C25-C24	1.40	1.38	C27-C26-N5	129.21	124.64	C27-C26-N5-C4	-4.82	-39.61
C25-C20	1.37	1.40	C28-C27-C26	125.10	124.61	C28-C27-C26-N5	-178.99	-178.90
Br2-C23	1.90	1.90	C29-C28-C27	121.65	123.60	C29-C28-C27-C26	11.86	11.05
C26-N5	1.41	1.42	C30-C29-C28	120.11	121.11	C30-C29-C28-C27	176.95	179.01
C27-C26	1.34	1.33	C31-C30-C29	119.54	119.15	C31-C30-C29-C28	1.41	0.38
C28-C27	1.48	1.46	C32-C31-C30	120.17	121.33	C32-C31-C30-C29	-2.39	-0.25
C29-C28	1.38	1.40	C33-C30-C29	119.24	118.77	C33-C32-C31-C30	1.53	0.28
C30-C29	1.36	1.40	Br3-C31-C30	119.20	119.25	Br3-C31-C30-C29	-179.21	-179.80
C31-C30	1.40	1.37						
C32-C31	1.40	1.37						
C33-C32	1.38	1.42						
C33-C28	1.40	1.39						
Br3-C31	1.90	1.90						



8. TD-DFT Calculations at the MPW1PW91/6-31G* Level in CH_2Cl_2 for 3-NPh_2, 4-NPh_2 and 4-Br

Table S3. Energy (nm) and composition of the allowed electronic excitation energies (oscillator strength f ≥ 0.035) for **3-NPh_2, 4-NPh_2 and 4-Br** (B3LYP/6-31G*) in CH_2Cl_2.

Compound	λ_{max} [a] (nm)	λ_{calc} [a] (nm)	Oscillator strength (*f*)	Main transitions (weight)[b]
3-NPh_2	417	417	2.64	H-0 → L+0 (+51%); H-2 → L+2 (+21%); H-1 → L+1 (14%)
		416	2.65	H-1 → L+0 (+31%); H-2 → L+1 (+24%); H-1 → L+2 (20%); H-0 → L+1 (20%)
	322	319	0.96	H-4 → L+0 (+35%); H-3 → L+1 (30%); H-4 → L+2 (19%)
4-NPh_2	368	367	1.52	H-0 → L+1 (+56%); H-1 → L+0 (+19%); H-2 → L+2 (14%)
		366	1.50	H-1 → L+2 (+37%); H-0 → L+0 (+26%); H-2 → L+0 (18%);
4-Br	291	296	1.14	H-0 → L+0 (+61%) ; H-1 → L+0 (+24%)
		294	1.36	H-0 → L+1 (+64%) ; H-1 → L+1 (+17%)
	218	218	0.18	H-4 → L+0 (+40%); H-1 → L+3 (+19%)

[a] λ_{max} is the maximum absorption wavelength read on the simulated spectra, whereas λ_{calc} are the computed wavelengths given by the TD-DFT computations which were used to plot the simulated spectra. [b] Participation of transitions of less than 10% in a given excitation are not reported.

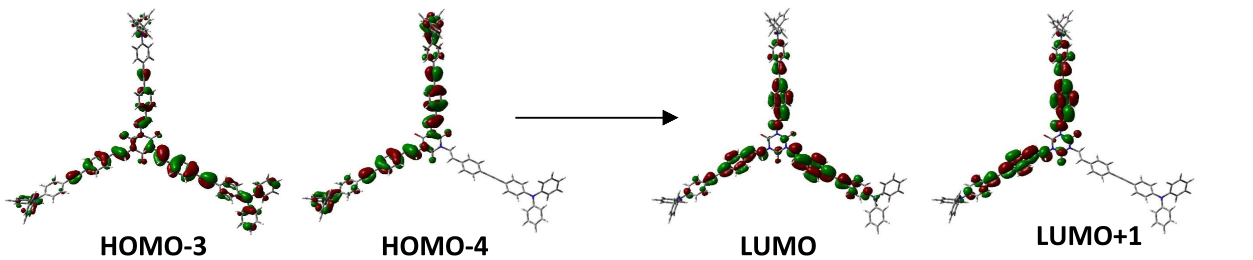


Figure S7. Plots of the frontier molecular orbitals for **3-NPh_2** primarily involved in the second allowed transition. Contour values are ± 0.03 $(e/bohr^3)^{1/2}$.

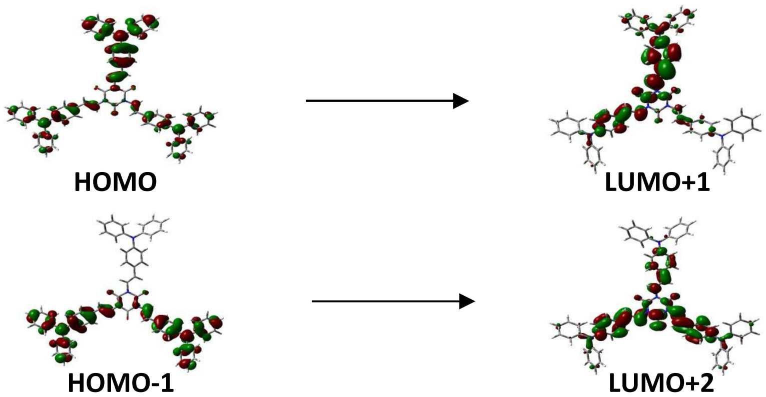


Figure S8. Plots of the frontier molecular orbitals for **4-NPh_2** primarily involved in the first allowed transition composing the first absorption. Contour values are ± 0.03 $(e/bohr^3)^{1/2}$.

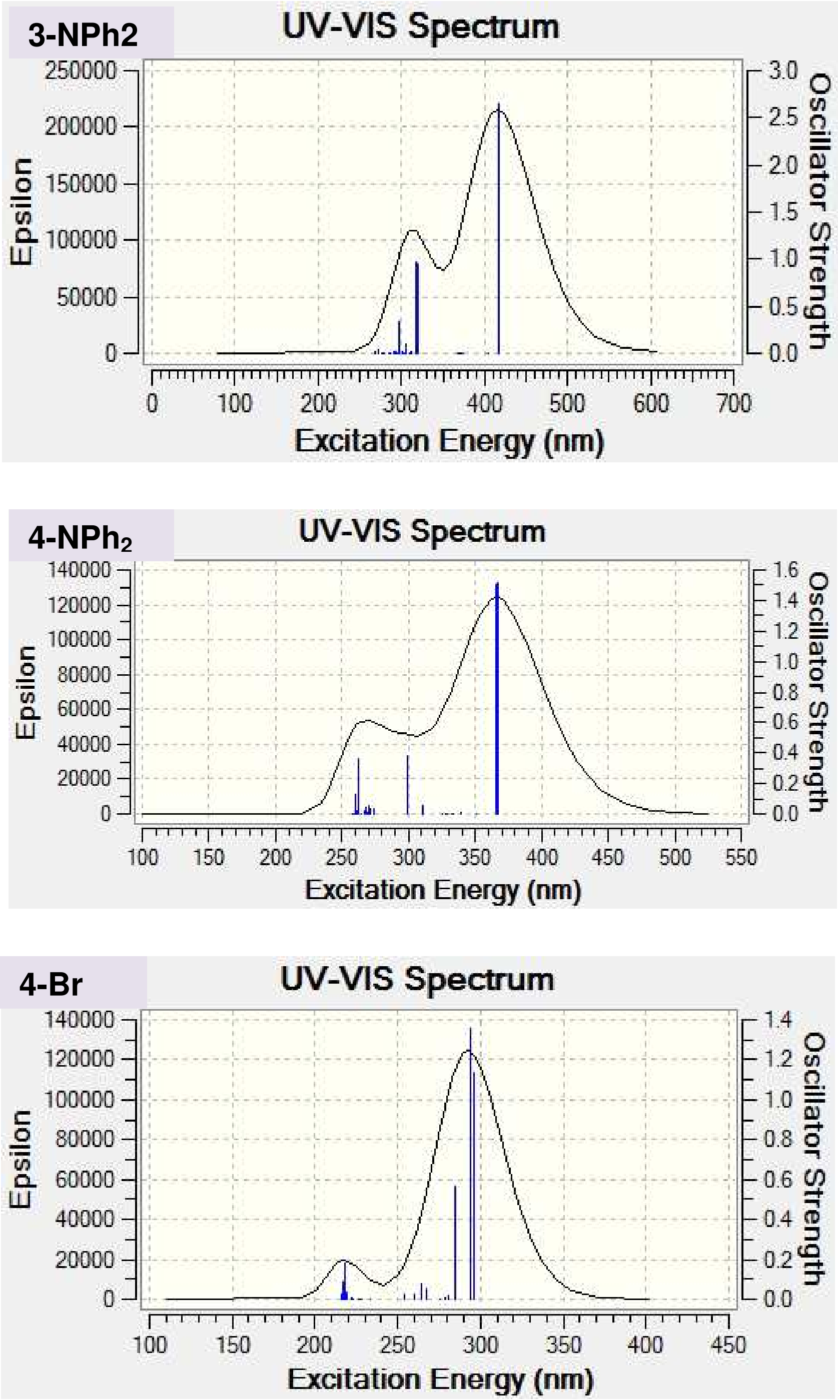


Figure S9. TD-DFT-computed (sticks) spectra for **3-NPh$_2$, 4-NPh$_2$** and **4-Br**.