

Supplementary Information

Effect of molecular architecture in two-photon absorption: from octupolar molecules to polymers and hybrid polymer nanoparticles based in 1,3,5-triazine

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S1. Experimental details of the synthesis

Materials

The catalyst of Pd(PPh₃)₄ was synthesized in our own lab. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry argon. Triethylamine (TEA) was dried over and distilled from KOH and oxygen was removed before use. 1,4-Dibromo-2,5-bisdodecyloxybenzene [1], 2,7-dibromo-9H-carbazole [2], 2,7-dibromo-9H-fluorene [3] was synthesized as described in the corresponding references.

Instrumentation

¹H-NMR and ¹³C-NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS, δ = 0 ppm) as internal standard. EI-MS spectra were recorded with a VJ-ZAB-3F-Mass spectrometer. Elemental analysis was performed with a CARLOERBA-1106 micro-elemental analyzer. Gel permeation chromatography (GPC) analysis was performed on an Agilent 1100 series HPLC system equipped with a G1326A refractive index detector, in which polystyrene standards were used as calibration standards and THF was used as an eluent and the flow rate was 1.0 mL/min.

Synthesis and characterization

Monomers:

1,4-dibromo-2,5-bisdodecyloxybenzene (1) [4]: The white solids (yield, 97%). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.90 (t, 6H), 1.29 (b, 32H), 1.50 (m, 4H), 1.82 (m, 4H), 3.95 (t, 4H), 7.08 (s, 2H).

2,7-dibromo-9-dodecylcarbazole (2) [5]: The white solids (yield, 84%). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.89 (t, 3H), 1.24 (m, 18H), 1.82 (m, 2H), 4.24 (t, 2H), 7.28 (d, 2H), 7.530 d, 2H), 8.13 (s, 1H).

2,7-dibromo-9,9-dihexylfluorene (3) [6]. The white crystals (yield, 87 %). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.59 (m, 4H), 0.79 (t, 6H), 1.06-1.17 (m, 12H), 1.89-1.95 (m, 4H), 7.42-7.52 (m, 6H).

2,5-bis-dodecyloxy-1,4-diethynyl-benzene (4) [3]: The yellow crystals (yield, 52 %). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.80 (t, 6H), 1.18-1.22 (m, 32H), 1.38 (m, 4H), 1.74 (m, 4H), 3.25 (s, 2H), 3.89 (t, 4H), 6.85 (s, 2H).

2,7-diethynyl-9-Dodecylcarbazole (5) [7]: The light yellow crystals (yield, 87 %). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.87 (t, 3H), 1.22 (m, 18H), 1.84 (m, 2H), 3.08 (s, 2H), 4.26 (t, 2H), 7.35 (d, 2H), 7.62 (d, 2H), 8.22 (s, 1H).

2,7-diethynyl-9,9-dihexylfluorene (6) [8]: The white solids (yield, 93 %). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.55 (m, 4H), 0.76 (t, 6H), 1.00-1.11 (m, 12H), 1.90-1.95 (m, 4H), 3.46 (s, 2H), 7.45-7.49 (m, 4H), 7.61 (d, 2H).

2,4,6-tris(thiophen-2-yl)-1,3,5-triazine (7) [9]: The pine needle crystals (yield, 85 %). ¹H-NMR (300Mz, CDCl₃, δ ppm): 7.22 (d, 3H), 7.63 (d, 3H), 8.29(d, 3H). ¹³C-NMR (75Mz, CDCl₃, δ ppm): 129.0, 132.5, 133.0, 142.2, 168.5.

2,4-bis(5-bromo-thiophen-2-yl)-6-(thiophen-2-yl)-1,3,5-triazine (8) [10]: To a solution of 7 (0.98 g, 3 mmol) in 10 mL DMF was added NBS (1.34 g, 7.5 mmol) in 5 mL DMF. The mixture was stirred at room temperature for 24 h and then was poured into 500 mL H₂O. The obtained precipitate was filtered. The product was purified by chromatography using petroleum ether as an eluent. Yield, 0.71 g (49%, white solid). ¹H-NMR (300Mz, CDCl₃, δ ppm): 7.17 (d, 2H), 7.21 (t, 1H), 7.63-7.65 (m, 1H), 7.99 (d, 2H), 8.23 (d, 1H). ¹³C-NMR (75Mz, CDCl₃, δ ppm): 120.7, 128.7, 131.8, 132.1, 132.2, 132.9, 141.2, 142.6, 166.93, 167.95. Anal. Calcd for C₁₅H₇N₃S₃Br₂: C, 37.13; H, 1.45; N, 8.66, S 19.82. Found: C, 37.55; H, 1.84; N, 8.33; S, 19.16. EI-MS: m/z = 485.0 (Calcd: 484.8).

General procedure for the preparation of polymers P1-P3 [11]: 8 (0.048g, 0.1mmol), the related diethynyl monomer (0.1 mmol), Pd(PPh₃)₄ (5 mg, 2 %), CuI (3 mg, 2 %) and PPh₃ (2 %) was dissolved in TEA (0.5 mL) and THF (10 mL) at argon atmosphere. The mixture was stirred at 35 °C for 3 days. Then the reaction mixture was dropped into 200 mL methanol through a cotton filter. The solid was collected and purified by precipitation into methanol for 3 times.

P1: The orange power. Yield: 60 mg (71%). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.84 (t, 6H), 1.21-1.43 (m, 32H), 1.87 (m, 4H), 4.068 (m, 4H), 7.03 (d, 2H), 7.18 (d, 1H), 7.34 (m, 2H), 7.65 (d, 1H), 8.17(m, 2H), 8.26 (m, 2H). ¹³C-NMR (75Mz, CDCl₃, δ ppm): 13.1, 21.7, 25.1, 28.4, 28.7, 30.9, 68.7, 87.6, 91.8, 112.9, 115.6, 116.57, 119.4, 127.5, 130.7, 131.6, 132.0, 141.2, 152.7, 166.0. Molecular weights: M_n = 6.66×10³ g/mol, M_w = 1.13 × 10⁴ g/mol, D = 1.70.

P2: The yellow power. Yield: 56 mg (80 %). ¹H-NMR (300Mz, CDCl₃, δ): 0.87 (t, 6H), 0.99-1.38 (m, 32H), 1.67-1.77 (m, 4H), 3.94-4.21 (m, 4H), 6.92-7.32 (m, 5H), 7.45-7.61 (m, 2H), 7.92-8.26 (m, 4H). ¹³C-NMR (75Mz, CDCl₃, δ ppm): 13.1, 21.7, 26.2, 27.9, 28.3, 28.6, 30.9, 42.2, 81.0, 96.9, 107.8, 112.4, 121.3, 123.3, 127.5, 127.8, 130.4, 130.5, 130.8, 139.5, 140.2, 141.5, 165.7. Molecular weights: M_n = 2.10 × 10³ g/mol, M_w = 3.77 × 10³ g/mol, D = 1.79.

P3: The yellow power. Yield: 66 mg (94%). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.64 (m, 4H), 0.79 (t, 6H), 1.09 (m, 12H), 2.02 (m, 4H), 7.38 (s, 2H), 7.55 (m, 4H), 7.65-7.71 (m, 3H), 8.19 (m, 1H), 8.28 (m, 1H). ¹³C-NMR (75Mz, CDCl₃, δ ppm): 13.0, 21.6, 22.8, 28.7, 30.5, 39.4, 54.4, 82.4, 96.2, 119.2, 120.3, 125.0, 127.5, 129.1, 129.8, 130.68, 130.70, 131.9, 140.2, 141.0, 150.3, 166.0. Molecular weights: M_n = 8.42 × 10³ g/mol, M_w = 1.79 × 10⁴ g/mol, D = 2.12.

Procedure for the preparation of polymer P4 [12]: 8 (0.048 g, 0.1 mmol), 9,9-di-n-hexylfluorene-2,7-bis(trimethyl-eneboronate) (0.050 g, 0.1 mmol), K₃PO₄·H₂O (0.23 g, 1 mmol), Pd(PPh₃)₄ (5 mg) was dissolved in THF/H₂O (8 mL/2 mL) at Ar atmosphere. The reaction mixture was stirred at 65 °C for 3 days, and then the reaction mixture was dropped into 200 mL methanol through a cotton filter. The solid was collected and recrystallized from methanol for 3 times. The product was obtained as greenish yellow power. Yield: 44 mg (63 %). ¹H-NMR (300Mz, CDCl₃, δ ppm): 0.82 (m, 10H), 1.18 (m, 12H), 2.16 (s, 4H), 7.50-7.72 (m, 10H), 7.37 (m, 3H). ¹³C-NMR (75 Mz, CDCl₃, δ ppm): 14.3, 22.9, 24.1, 29.9, 31.8, 40.6, 55.8, 120.67, 120.68, 124.6, 125.5, 128.7, 131.9, 132.5, 132.2, 140.1, 141.4, 141.9, 152.1, 152.3, 167.7. Molecular weights: M_n = 6.44 × 10³ g/mol, M_w = 1.26 × 10⁴ g/mol, D = 1.97.

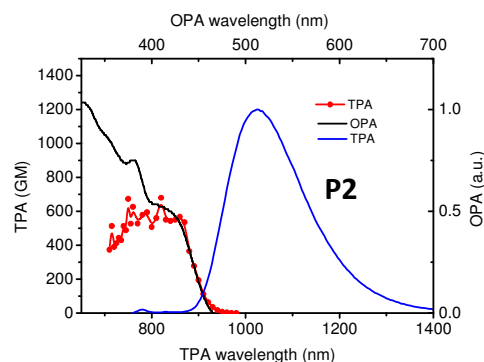


Figure S2. Two-photon absorption (TPA in GM) spectra of the product of the synthesis of polymers **P2** in THF compared with one photon absorption (OPA) and emission (OPE) in arbitrary units. Note that the estimated molecular weight gives on average 4 monomeric units per polymer chain

In **P2**, the delocalized π - π^* transition is observed as a shoulder at 410 nm, while the absorption maximum corresponds to a π - π^* transition localized in the triazine-thiophen core at 324 nm.[13] A third band is observed at 380 nm, which is assigned to an electronic transition localized in the carbazole group. The absorption spectrum of this particular batch of **P2** indicates that the structure does not exactly correspond to a linear polymer of alternating electron donor and acceptor units. This spectrum is also substantially different from the one published earlier.[10] Nevertheless, emission of **P2** does seem to come from well conjugated donor-acceptor units because this polymer shows the red-most emission band at 512 nm in good agreement with the emission at 509 nm reported earlier.

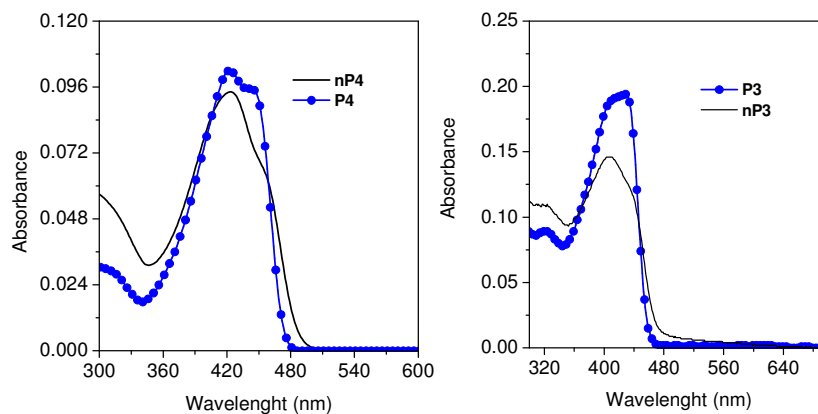


Figure S3. Comparison between the absorption spectra of **P3** and **P4** in the THF solution at the concentration of the initial THF/water mixture used in the preparation of the nanoparticles, and the spectra of the corresponding final nanoparticle dispersion in water. The 6% and 20% drop in the absorption maxima of **P4** and **P3**, respectively, is attributed to a loss of material.

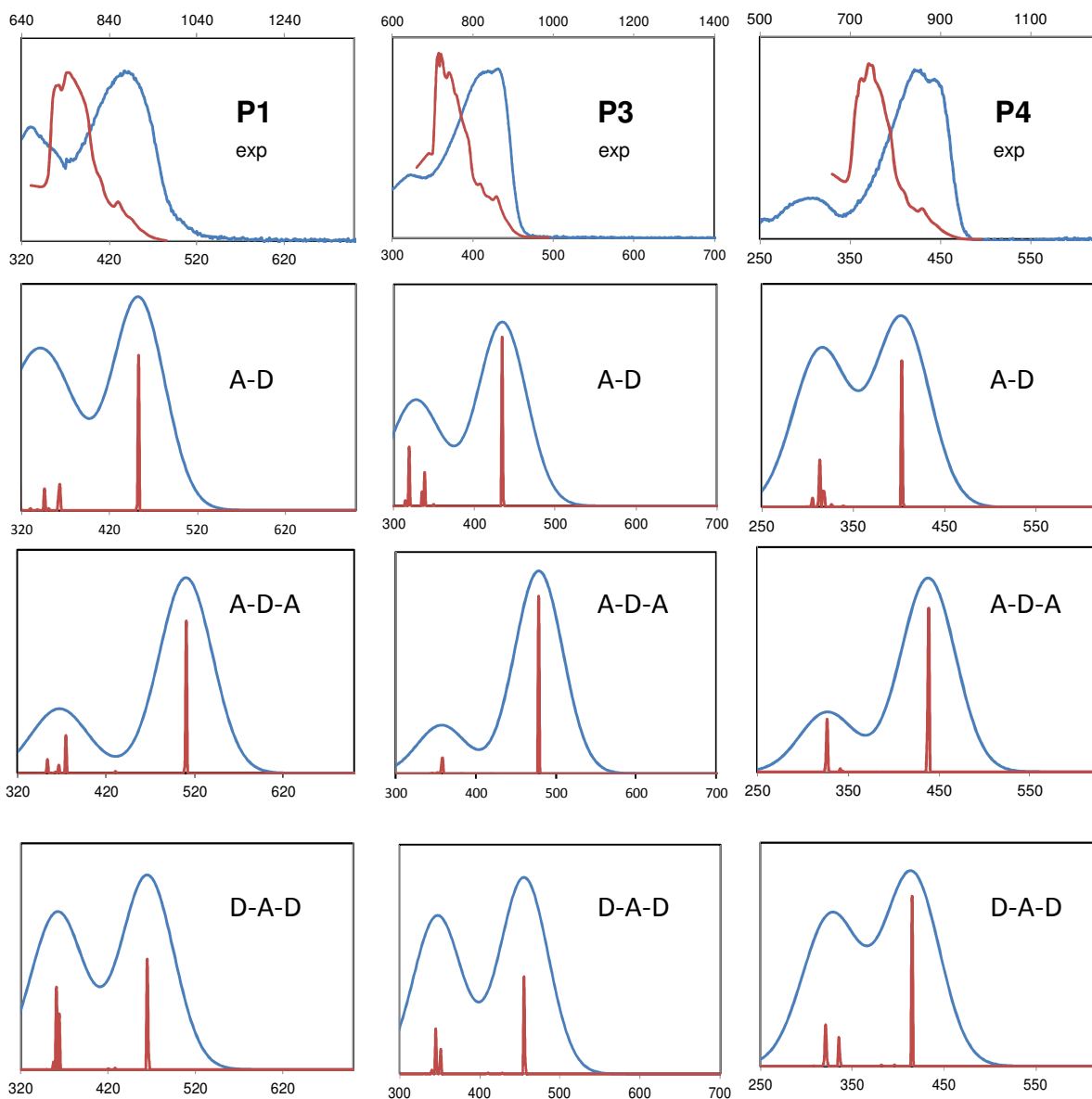
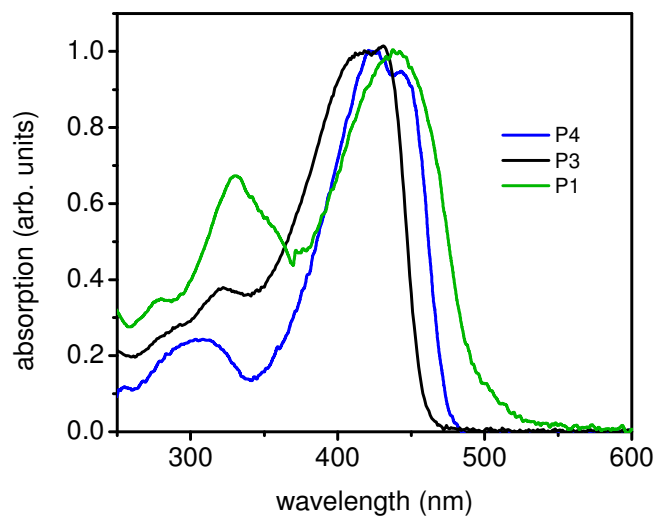


Figure S4. Experimental linear and two-photon absorption spectra in THF, and calculated absorption spectra for an A- π -D dipolar unit, and A- π -D- π -A and D- π -A- π -D quadrupolar units in vacuum at the B3LYP/6-31+G(d,p) level. Calculated spectra are plotted using 0.5 and 30 nm gaussian functions centred at the transition wavelength.



S5. Linear absorption spectra of the studied polymers in THF.

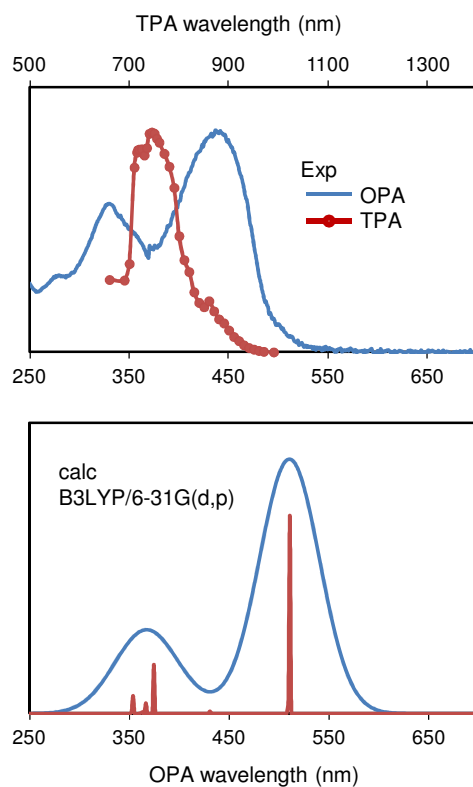


Figure S6. Experimental spectra of and calculated absorption spectra of **P1**: a) experimental linear and two-photon absorption spectra in THF, and b) simulated spectra in vacuum for a A- π -D- π -A quadrupolar unit using 0.5 and 30 nm gaussian functions

Table S7 - Molecular orbitals involved in the lower energy electronic transitions predicted at a TDDFT level for the quadrupolar monomer model of polymer **P1**, wavelength of the transition (nm), oscillator strength (f) and corresponding percentage contribution of each transition to the CI expansion.

A- π -D- π -A	Transition	λ (nm)	f	%
P1				
$S_0 \rightarrow S_1$	H->L	510	2.3017	49
$S_0 \rightarrow S_2$	H->L+1	431	0.0330	47
$S_0 \rightarrow S_3$	H->L+2	427	0.0001	48
$S_0 \rightarrow S_4$	H->L+3	426	0.0000	48
$S_0 \rightarrow S_5$	H-2->L	374	0.4247	48
$S_0 \rightarrow S_6$	H-1->L	367	0.0995	46

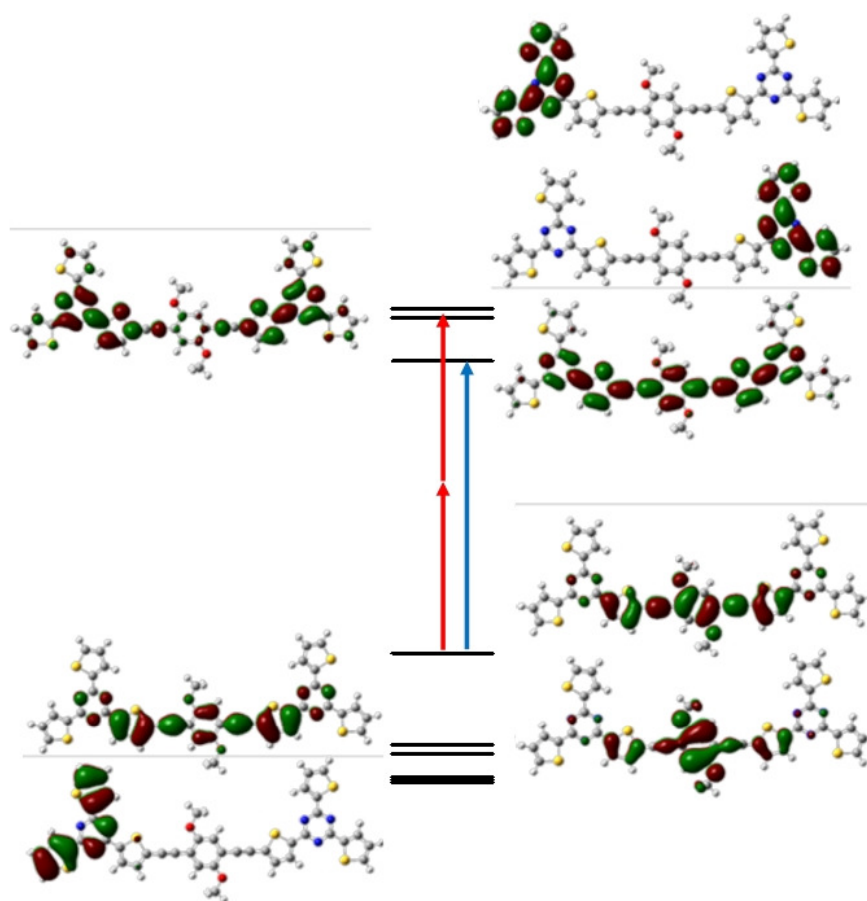


Figure S8. Isodensity surface of the frontier molecular orbitals in the quadrupolar monomer A- π -D- π -A model of polymers **P1** indicating (in blue) the H->L transition responsible for linear absorption and (in red) the H->L+1 transition that could be associated with biphotonic absorption. The degenerated H->L+2 and H->L+3 are also possible candidates for TPA. All three transition have a strong charge transfer character.

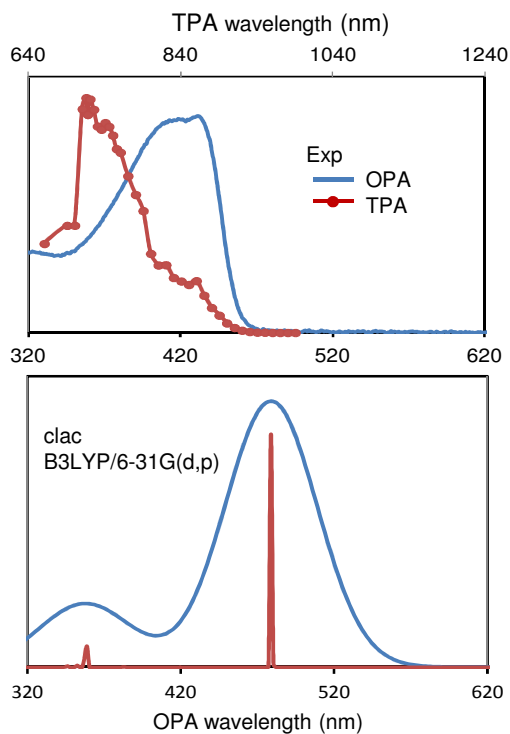


Figure S9. Experimental and calculated absorption spectra of **P3**: a) experimental linear and two-photon absorption spectra in THF, and b) simulated spectra in vacuum for a A- π -D- π -A quadrupolar unit using 0.5 and 30 nm gaussian functions

Table S10 - Molecular orbitals involved in the lower energy electronic transitions predicted at a TDDFT level for the quadrupolar monomer model of polymer **P3**, wavelength of the transition (nm), oscillator strength (f) and corresponding percentage contribution of each transition to the CI expansion.

A- π -D- π -A	Transition	λ (nm)	f	%
P3				
$S_0 \rightarrow S_1$	H->L	478	3.0910	96
$S_0 \rightarrow S_2$	H->L+1	419	0.0021	95
$S_0 \rightarrow S_3$	H->L+2	405	0.0000	91
$S_0 \rightarrow S_4$	H->L+3	405	0.0000	92
$S_0 \rightarrow S_5$	H-1->	382	0.0054	94
$S_0 \rightarrow S_6$	H-1->L+1	358	0.6854	78
	H->L+4			16

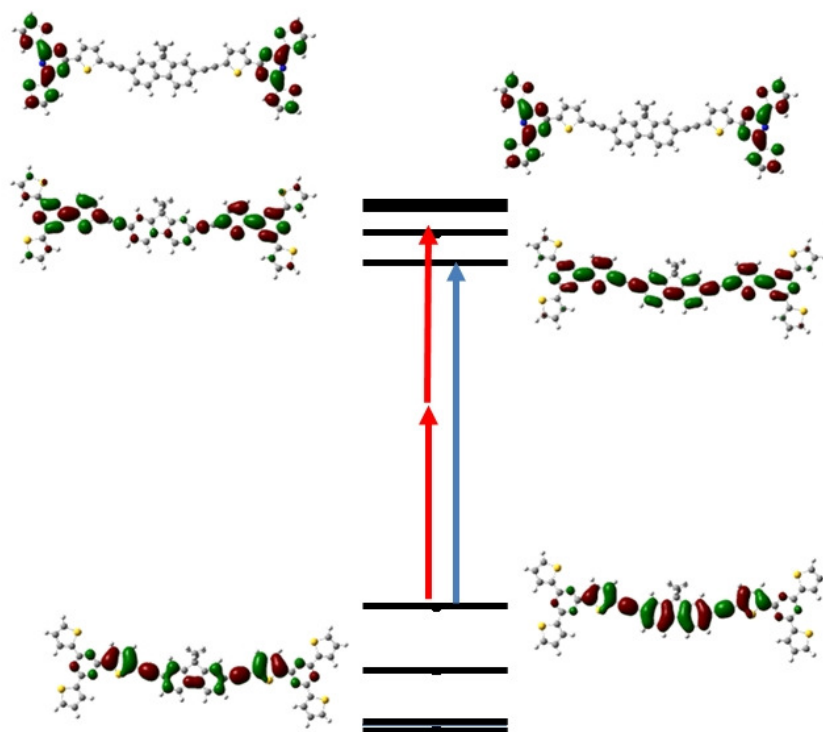


Figure S11. Isodensity surface of the frontier molecular orbitals in the quadrupolar A- π -D- π -A monomer model of polymers **P3** indicating (in blue) the H- \rightarrow L transition responsible for linear absorption and (in red) the H- \rightarrow L+1 transition that could be associated with biphotonic absorption. The degenerated H- \rightarrow L+2 and H- \rightarrow L+3 are also possible candidates for TPA. All three transition have a strong charge transfer character.

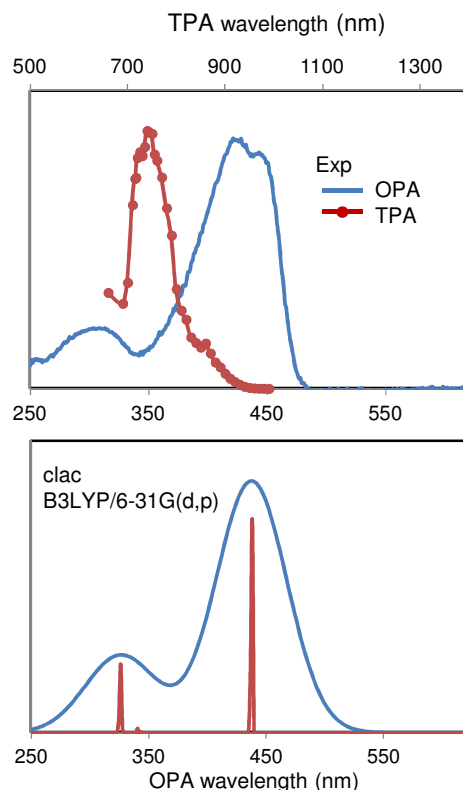


Figure S12. Experimental and calculated absorption spectra of **P4**: a) experimental linear and two-photon absorption spectra in THF, and b) simulated spectra in vacuum for a A- π -D- π -A quadrupolar unit using 0.5 and 30 nm gaussian functions

Table S13 - Molecular orbitals involved in the lower energy electronic transitions predicted at a TDDFT level for the quadrupolar monomer model of polymer **P4**, wavelength of the transition (nm), oscillator strength (f) and corresponding percentage contribution of each transition to the CI expansion.

A- π -D- π -A	Transition	λ (nm)	f	%
P4				
$S_0 \rightarrow S_1$	H->L	438	2.265	97
$S_0 \rightarrow S_2$	H->L+3	392	0	92
$S_0 \rightarrow S_3$	H->L+2	392	0	93
$S_0 \rightarrow S_4$	H->L+1	388	0.004	96
$S_0 \rightarrow S_5$	H-1->L	344	0.007	92
$S_0 \rightarrow S_6$	H-2->L	341	0.004	59
	H-3->L+1			21
$S_0 \rightarrow S_7$	H-3->L	341	0.021	58
	H-2->L+1			20
$S_0 \rightarrow S_8$	H-4->L	328	0.017	69
	H-5->L+1			15
$S_0 \rightarrow S_9$	H-5->L	328	0.000	75
	H-4->L+1			16

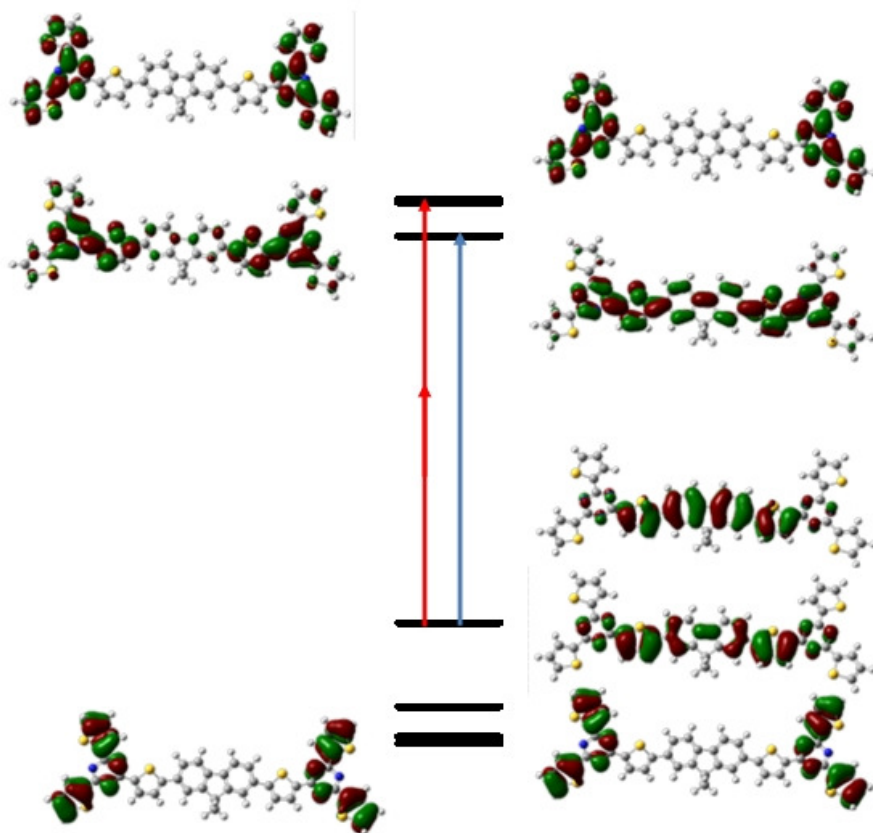
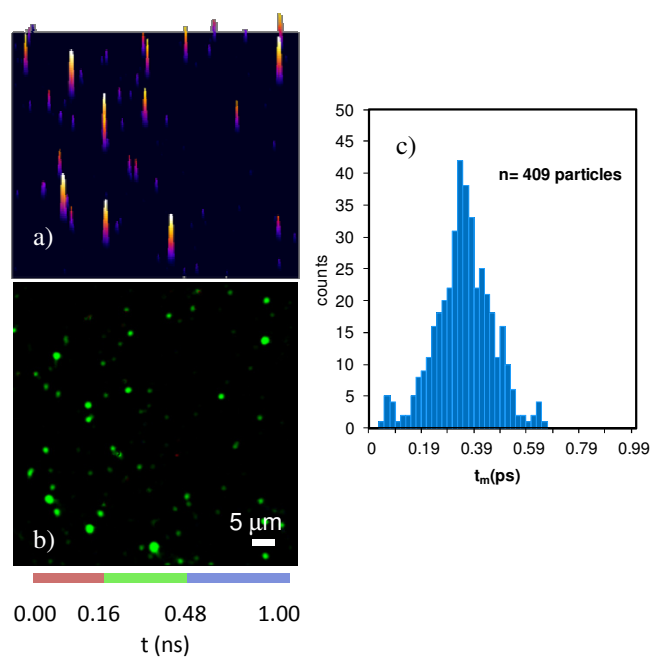


Table S14. Isodensity surface of the frontier molecular orbitals in the quadrupolar monomer A- π -D- π -A model of polymers **P4** indicating (in blue) the H->L transition responsible for linear absorption and (in red) the degenerated H->L+1, H->L+2 and H->L+3 transitions that could be associated with biphotonic absorption.



S15. Fluorescence microscopy imaging of isolated nanoparticles of **P3**: a) confocal microscopy image obtained with excitation at 458 nm by collecting the fluorescence emission in the 475-600 nm region, b) fluorescence lifetime image, and c) corresponding lifetime distribution. Note that in the FLIM image the intensity of the brightest particles is saturated so that the lowest intensity particles can be more clearly shown.

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