Sequential double second-order nonlinear optical switch by an acido-triggered photochromic cyclometallated platinum(II) complex

Julien Boixel,[a] Véronique Guerchais,[a*] Hubert Le Bozec,[a] Agisilaos Chantzis,[b,c] Denis Jacquemin,[b,c*] Alessia Colombo,[d*] Claudia Dragonetti,[d,e] Daniele Marinotto,[e] and Dominique Roberto[d,e]

[a] *UMR 6226 CNRS-Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Campus de Beaulieu, 35042 Rennes, France. E-mail: veronique.guerchais@univ-rennes1.fr;*
[b] *UMR CNRS 6230, Université de Nantes, CEISAM, 44322 Nantes cedex 3, France. E-mail: denis.jacquemin@univ-nantes.fr;*
[c] *Institut Universitaire de France, IUF, 103, Blvd St Michel, F-75005 Paris cedex 5, France;*
[d] *Dipartimento di Chimica dell'Università degli Studi di Milano, UdR dell'INSTM, 20133 Milano, Italy. E-mail: alessia.colombo@unimi.it;*
[e] *ISTM-CNR, 20133 Milano, Italy.*

Contents

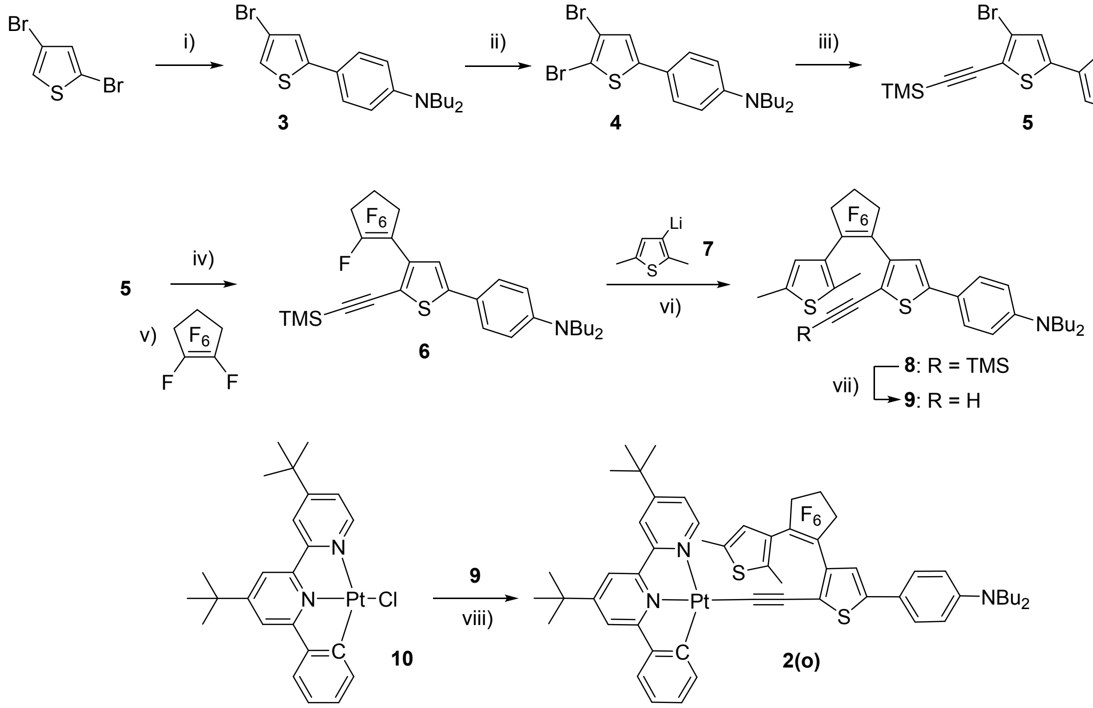
page

1. Experimental Section

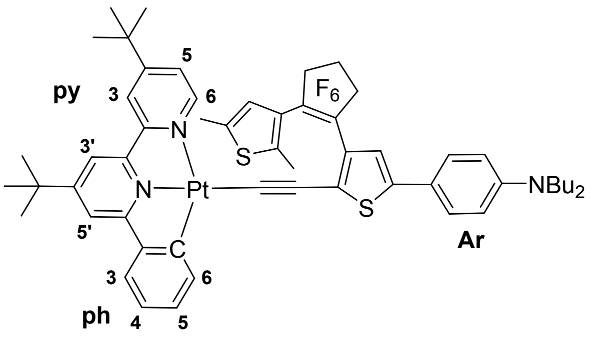
3. Computational data

1-Experimental section

General. All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. Compounds 3-bromo-2,5-dimethylthiophene[1] and **10**[2] were prepared following reported procedures. NMR spectra were recorded on Bruker, AV 400 spectrometers. ^{1}H and ^{13}C chemical shifts are determined by reference to residual ^{1}H and ^{13}C solvent signals. Elemental Analysis were performed at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. UV/vis absorption spectra were recorded using Specord 205 UV-Vis-NIR spectrophotometer using quartz cuvettes of 1 cm pathlength.



Scheme S1. Stepwise synthesis of the platinum complex **2(o)**. i) THF, *p*-$Bu_2N-C_6H_4-B(OBu_2)$, -78°, $Pd(PPh_3)_4$, Na_2CO_3, 100°C, 12h. ii) N-bromosuccinimide, THF, 12h. iii) $Pd(PPh_3)_2Cl_2$, CuI, TMSA, THF, Et_3N, 60°C, 12h. iv) ^{n}Buli, THF, vi) -78°C to r.t., 12h. vii) THF, -78°C to r.t., 12h. vi) CH_2Cl_2, MeOH, K_2CO_3, r.t., 3h. viii) CH_2Cl_2, CuI, 30°C, 12h.



Scheme S2. Numbering of the complex **2(o)**.

Procedures for the synthesis of complex 2(o).

Synthesis of 4-(4-bromothiophen-2-yl)-*N*,*N*-dibutylaniline, 3. To a dry THF solution (40 mL) of 4-bromo-*N*,*N*-dibutylaniline (2.84 g, 10 mmol) at -80°C, ^{n}butyllithium in hexane (8 mL, 12 mmol) was added under argon atmosphere. After 30 minutes, tributylborate (2.97 mL, 11 mmol) was added. Then the reaction mixture was warm up to 0°C, and transferred by cannula into an aqueous solution (10 mL) of 2,4-dibromothiophene (2.5 g, 10 mmol) with Na_2CO_3 (3g, 28 mmol) and $Pd(PPh)_3Cl_2$ (0.140 g, 0.20 mmol). The heterogeneous solution was heated at 100°C for 12h. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 and washed with brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (SiO_2, petroleum ether) to afford **3** (58 %, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 7.01 (2H, thio), 6.63 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.30 (t, $J_{H\text{-}H}$ = 8 Hz, 4H, ^{n}Bu$_2$), 1.59 (m, 4H, ^{n}Bu$_2$), 1.37 (m, 4H, ^{n}Bu$_2$), 0.97 (t, $J_{H\text{-}H}$ = 8 Hz, 6H, ^{n}Bu$_2$). ^{13}C [^{1}H] NMR (100 MHz, $CDCl_3$): 148.4, 146.7, 126.7, 122.6, 119.7, 114.2, 111.7, 106.8, 50.8, 29.5, 20.4, 14.1. Elemental Analysis: Calcd. for $C_{18}H_{24}NBrS$: C, 59.01; H, 6.60; N, 3.82. Found: C, 58.97; H, 6.67; N, 3.83.

Synthesis of 4-(4,5-dibromothiophen-2-yl)-*N*,*N*-dibutylaniline, 4. In a THF solution (100 mL) of **3** (2.1 g, 5.73 mmol) at 0°C, a THF solution (50 mL) of N-bromosuccinimide (1.07 g, 6.02 mmol) was added dropwise. Then, the reaction mixture was stirred at room temperature overnight. After addition of a $Na_2S_2O_3$ saturated solution (50 mL) and extraction with diethyl ether, the organic layer was dried over $MgSO_4$, filtered and concentrated to dryness. **4** was isolated as a colorless solid (67 %). ^{1}H NMR (400 MHz, $CDCl_3$): 7.35 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 6.94 (s, 1H, thio), 6.65 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.33 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, ^{n}Bu$_2$), 1.63 (m, 4H, ^{n}Bu$_2$), 1.42 (m, 4H, ^{n}Bu$_2$), 1.03 (t, $J_{H\text{-}H}$ = 8 Hz, 6H, ^{n}Bu$_2$). ^{13}C [^{1}H] NMR (100 MHz, $CDCl_3$): 148.3, 146.8, 127.0, 123.0, 120.4, 119.5, 111.7, 110.3, 50.9, 29.6, 20.5 14.2. Elemental Analysis: Calcd. for $C_{18}H_{23}NBr_2S$: C, 48.56; H, 5.21; N, 3.15. Found: C, 48.70; H, 5.29; N, 3.08.

Synthesis of 4-(4-bromo-5-((trimethylsilyl)ethynyl)thiophen-2-yl)-*N*,*N*-dibutylaniline, 5. To a dry THF (50 mL) and Et_3N (15 mL) solution of **4** (2.8 g, 6.30 mmol), $Pd(PPh_3)_2Cl_2$ (88 mg, 0.13 mmol) and CuI (24 mg, 0.13 mmol), trimethylsilylacetylene (0.986 mL, 1.88 mmol) was added dropwise. The reaction mixture was heating at 60 °C overnight. After cooling down to room temperature, the reaction was extracted with brine and the organic phase was dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether : CH_2Cl_2, 9 : 1) to afford **5** (82 %, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): 7.37 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 6.95 (s, 1H, thio), 6.62 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.30 (t, $J_{H\text{-}H}$ = 8 Hz, 4H, ^{n}Bu$_2$), 1.59 (m, 4H, ^{n}Bu$_2$), 1.37 (m, 4H, ^{n}Bu$_2$), 0.98 (t, $J_{H\text{-}H}$ = 8 Hz, 6H, ^{n}Bu$_2$), 0.29 (s, 9H, TMS). ^{13}C [^{1}H] NMR (100 MHz, $CDCl_3$): 148.4, 146.7, 126.7, 122.6, 119.7, 114.2, 111.7, 106.8, 50.8, 29.5, 20.4, 14.1, -0.29. Elemental Analysis: Calcd. for $C_{23}H_{32}NBrSSi$: C, 59.01; H, 6.60; N, 3.82. Found: C, 58.97; H, 6.67; N, 3.83.

Synthesis of 4-(4-heptafluorocyclopentene-5-((trimethylsilyl)ethynyl)thiophen-2-yl)-N,N-dibutylaniline, 6. To a dry THF (40 mL) solution of **5** (1.8 g, 5.20 mmol) at -78°C was added dropwise ^{n}butyllithium (3.8 mL, 5.71 mmol). The reaction was stirred at -78°C for 1h and transferred by cannula into a THF solution (20 mL) of perfluorocyclopentene (1.86 mL, 0.02 mol) at -78°C. The reaction mixture was warm up to room temperature under stirring overnight. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 and washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (SiO_2, petroleum ether) to afford **6** (47 %, orange oil). ^{1}H NMR (400 MHz, $CDCl_3$): 7.41 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 7.09 (s, 1H, thio), 6.63 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.31 (d, $J_{H\text{-}H}$ = 8 Hz, 4H, ^{n}Bu$_2$), 1.59 (m, 4H, ^{n}Bu$_2$), 1.37 (m, 4H, ^{n}Bu$_2$), 0.98 (t, $J_{H\text{-}H}$ = 8 Hz, 6H, ^{n}Bu$_2$), 0.25 (s, 9H, TMS). ^{13}C [^{1}H] NMR (100 MHz, $CDCl_3$): 148.7, 147.8, 127.4, 123.1, 119.5, 118.7, 111.8, 106.4, 95.6, 50.9, 41.5, 29.5, 27.8, 22.8, 20.5, 14.1, -0.29. Elemental Analysis: Calcd. for $C_{28}H_{32}NF_7SiS$: C, 58.42; H, 5.60; N, 2.43. Found: C, 58.37; H, 5.49; N, 2.36.

Synthesis of 5-(4-*N*,*N*-dibutylaniline)-3-(2-(2,5-dimethylthiophene-3-yl)-hexafluorocyclopent-1-en-1-yl)thiophene-2-(trimethylsilyl)ethynyl, 8. To a THF solution (10 mL) of compound **6** (215 mg, 1.12 mmol) at -80ºC, ^{n}butyllithium in hexane (1.5 M, 0.8 ml, 1.22 mmol) was added. After 30 min, a THF solution (10 mL) of **7** (590 mg, 1.02 mmol) was added. The reaction mixture was stirred at -80°C for 30 min then warming up to r.t. for 15h. The solvents were removed under vacuum and the crude product was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 9:1) (0.305 g, 45% yield, orange powder). ^{1}H NMR (400 MHz, $CDCl_3$): 7.37 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 6.99 (s, 1H, thio), 6.76 (s, 1H, thio), 6.62 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.30 (d, $J_{H\text{-}H}$ = 8 Hz, 4H, ^{n}Bu$_2$), 2.42 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.58 (m, 4H, ^{n}Bu$_2$), 1.37 (m, 4H, ^{n}Bu$_2$), 0.98 (t, $J_{H\text{-}H}$= 8 Hz, 6H, ^{n}Bu$_2$), 0.25 (s, 9H, TMS). ^{13}C [^{1}H] NMR (100 MHz, $CDCl_3$): 148.7, 147.8, 127.4, 119.5, 118.7, 111.8, 50.9, 29.5, 22.8, 20.5, 14.1, -0.3. Elemental Analysis: Calcd. for $C_{34}H_{39}F_6NS_2Si$: C, 61.14; H, 5.89; N, 2.10. Found: C, 60.99; H, 5.89; N, 1.94.

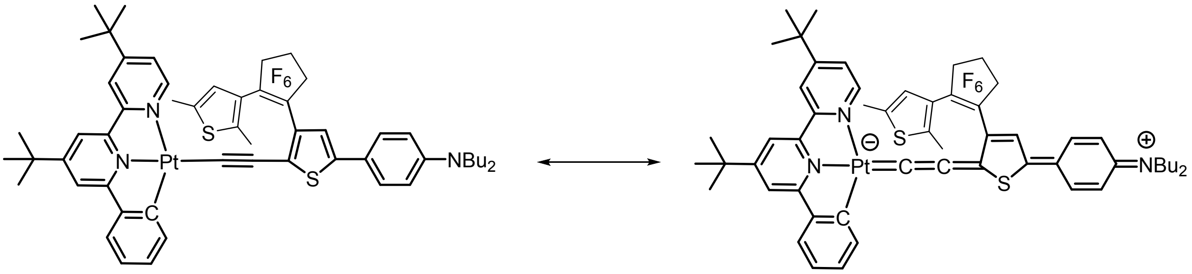
Synthesis of 5-(4-*N*,*N*-dibutylaniline)-3-(2-(2,5-dimethylthiophene-3-yl)-hexafluorocyclopent-1-en-1-yl)thiophene-2-ethynyl, 9. Compound **8** (0.300 g, 0.45 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and MeOH (5 mL). Potassium carbonate (0.620 g, 4.5 mmol) was then added and the reaction mixture was stirred at room temperature for 3 hours. After extraction with brine, the organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum to yield **9** as orange oil (0.250 g, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$): 7.39 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 7.06 (s, 1H, thio), 6.70 (s, 1H, thio), 6.63 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.34 (s, 1H, ≡CH), 3.30 (d, $J_{H\text{-}H}$ = 8 Hz, 4H, ^{n}Bu$_2$), 2.41 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.58 (m, 4H, ^{n}Bu$_2$), 1.38 (m, 4H, ^{n}Bu$_2$), 0.97 (t, $J_{H\text{-}H}$= 8 Hz, 6H, ^{n}Bu$_2$). Elemental Analysis: Calcd. for $C_{31}H_{31}NF_6S_2.1/4CH_2Cl_2$: C, 60.84; H, 5.15; N, 2.27. Found: C, 60.55; H, 5.15; N, 2.06.

Synthesis of complex 2(o). To a CH_2Cl_2/Et_3N (3/2: 15mL) solution of 4,4'-di(*tert*-butyl)-6-phenyl-2,2'-bipyridine platinum chloride **10** (0.289 g, 0.50 mmol), **9** (0.200 g, 0.34 mmol) and CuI (0.006 g, 0.03 mmol) were added. After 15 h of stirring at 30ºC, the mixture was extracted with CH_2Cl_2 and washed with water. The organic layers were dried over $MgSO_4$, filtered and concentred under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2; 6:4) to afford **2(o)** as an orange powder (0.206 g, 54 %). ^{1}H NMR (400 MHz, $CDCl_3$): 8.65 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Py6), 7.81 (s, 1H, Py3), 7.57 (s, 1H, Py3'), 7.54 (s, 1H, Py5'), 7.45 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ph6), 7.44 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Py5), 7.34 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ph3), 7.29 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 7.00 (m, 2H, Ph4/5), 6.89 (s, 1H, thio), 6.64 (s, 1H, thio), 6.55 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar), 3.21 (d, $J_{H\text{-}H}$ = 8 Hz, 4H, ^{n}Bu$_2$), 1.93 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.50 (m, 4H, ^{n}Bu$_2$), 1.37 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu), 1.29 (m, 4H, ^{n}Bu$_2$), 0.88 (t, $J_{H\text{-}H}$ = 8 Hz, 6H, ^{n}Bu$_2$). ^{13}C [^{1}H] NMR (100 MHz, $CDCl_3$): 165.3, 164.5, 165.4, 158.6, 155.0, 151.8, 148.5, 147.8, 143.2, 142.0, 136.6, 139.1, 136.9, 131.5, 127.1, 126.9, 126.0, 125.3, 125.2, 124.6, 124.0, 121.3, 120.1, 119.5, 116.3, 115.6, 112.3, 51.3, 36.5, 36.2, 30.8, 30.6, 30.0, 20.9, 15.2, 14.9, 14.4. Elemental Analysis: Calcd. for $C_{55}H_{57}N_3F_6S_2Pt$: C, 58.29; H, 5.07; N, 3.71. Found: C, 58.26; H, 5.25; N, 3.40.

Table S1. UV-visible absorption data of complexes **2(o)** and **2H⁺** in their open and closed forms.

complex	$\lambda_{abs}{}^{a}$ [nm] (ε x 10^3[L M^{-1}cm^{-1}]) *Open form*	$\lambda_{abs}{}^{a,b}$ [nm] *Closed form*
2	362 (28.0), 423 (10.0), 483 (7.0)	/
$2H^+$	332 (17.3), 440 (0.9)	343, 380, 585

[a] in ≈ 1.5 x 10^{-5} M CH_2Cl_2 solution at 298 K. [b] λ_{irr} = 350 nm.



Scheme S3. Possible resonance structures of **2(o)**.

2-EFISH measurements

All EFISH measurements were carried out at the Dipartimento di Chimica of the Università degli Studi di Milano, working in CH_2Cl_2 solutions at a concentration of 1 x 10^{-3} M, with a non-resonant incident wavelength of 1.907 μm, obtained by Raman-shifting the fundamental 1.064 μm wavelength produced by a Q-switched, mode-locked Nd^{3+}:YAG laser. The $\mu\beta_{EFISH}$ values reported are the mean values of 16 successive measurements performed on the same sample. The sign of μβ is determined by comparison with the reference solvent (CH_2Cl_2). This technique can provide direct information on the intrinsic molecular NLO properties, through equation 1:

$$\gamma_{EFISH} = (\mu\beta_{EFISH}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \qquad (1)$$

where $\mu\beta_{EFISH}$ /5kT is the dipolar orientational contribution to the molecular nonlinearity, and $\gamma(-2\omega; \omega, \omega, 0)$, the third order polarizability is a purely electronic cubic contribution to γ_{EFISH} which can usually be neglected when studying the second-order NLO properties of dipolar compounds.

3-Computational data

A. Computational Details

Quantum mechanical calculations based on the (TD)-DFT method were performed using Gaussian 09 suite of programs[3] using the pruned "ultrafine" (99,590) integration grid for all calculations and applying the IEF variant of the polarizable continuum model (PCM) to simulate the solvent (CH_2Cl_2). Ground state (GS) geometry optimizations relying on the Berny-GEDIIS algorithm[4] and using tight convergence criteria (1.0 × 10–5 a.u. for the RMS force) were performed at the PBE0//LANLDZP[5,6]/6-31G(d)[7] level of theory. The 6-31G(d) basis set, whenever it appears in the basis set description, has been used solely for boron since for this atom a LANL2DZP basis set does not exist. Subsequent harmonic frequency calculations and Natural Bond Orbital (NBO) population analyses at the same level of theory were performed so as to validate that the obtained structures correspond to an energy minimum (absence of negative frequencies) and to compute atomic partial charges, respectively. For the geometry optimizations, frequency calculations and NBO analyses the equilibrium PCM limit was adopted.

For an estimation of the wavelengths of maximal absorption (λ_{max}) of the various absorption bands, the linear response time-dependent density functional theory (TD-DFT) was employed at the PBE0//LAN2DZP/6-31G(d) level of theory. The vertical approximation was used and the transition energies were computed as $\Delta E^{abs} = E(S_n,\mathbf{R}_{GS}) - E(S_0,\mathbf{R}_{GS})$, where the first and second term correspond to the S_n and S_0 electronic energies respectively, both evaluated at the optimized ground state geometry, $\mathbf{R}_{GS}$. For the computation of transition energies the nonequilibrium linear-response PCM method was adopted.

For analyzing the nature of the $S_0 \rightarrow S_n$ electronic transitions, a Natural Transition Orbital (NTO) analysis has been performed as implemented in Gaussian 09 and the dominating NTO orbital pairs were visualized using GaussView 5.0 program using a 0.03 a.u. isovalue contour threshold. NTOs are computed by applying a unitary transformation to the occupied and virtual self-consistent field (SCF) spin orbitals. This procedure results in a number of NTO pairs (one occupied and one virtual) that can be used to get insights into the nature of the electronic transition being analyzed. The most important advantage of the formalism is that an electronic transition is readily attributed, for the majority of cases, to (at most) two NTO pairs that qualitatively depict the electron density reorganization due to the excitation. This analysis is proven to be a useful tool when the nature of the TD-DFT transition of interest involves an excited state that is not dominated by one singly excited configuration.

For the computation of the first hyperpolarizability tensor components as well as the vector components of the ground state dipole moment the widely employed long-range corrected ωB97X-D functional was used, which has shown very good performance in the theoretical prediction of NLO properties. The following definitions have been used:[8]

$$\mu = \mu_{tot} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \qquad (2)$$

$$\beta_{EFISH} \propto \beta_{//} = \frac{3}{5}\sum_i \frac{\mu_i}{\mu_{tot}} \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad (3)$$

where β_{EFISH} is the experimentally determined projection on the permanent dipole moment axis of the vectorial part of the first hyperpolarizability tensor, while the computed quantities μ_i, μ_{TOT} and β_{ijk} demote the *i* component of the computed dipole moment, its norm and the various components of the first hyperpolarizability tensor, respectively. The LANL2DZP/6-31G(d) basis sets were used and all properties were computed analytically according to the Taylor or “T” convention. Test calculations performed with the def2-SVPD basis set reveal only minor variations of the hyperpolarizability. While for a quantitative comparison between theory and experiment the conventions used by the experimentalists for the definition of the NLO properties must be taken into account, they lead to the same qualitative conclusions if they are consistently employed for all studied systems. Since our purpose in this work is to draw qualitative conclusions, these conventions are not taken into account.

B. Additional theoretical data

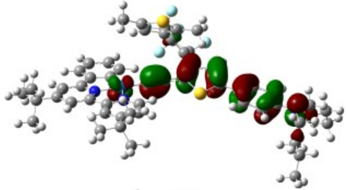
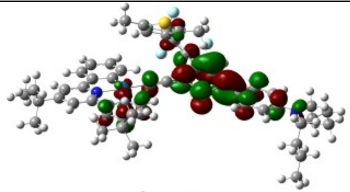
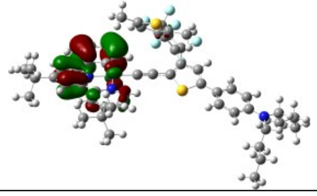
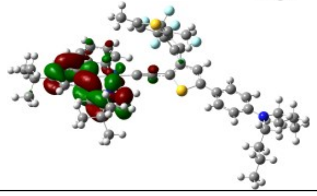
λ^{Theo} (nm)	**2(o)** Occupied	**2(o)** Virtual
372		
327		

Figure S1. NTO pairs corresponding to transitions belonging to the high-energy part of the UV-vis spectrum of system **2(o)** (0.03 isovalue used).

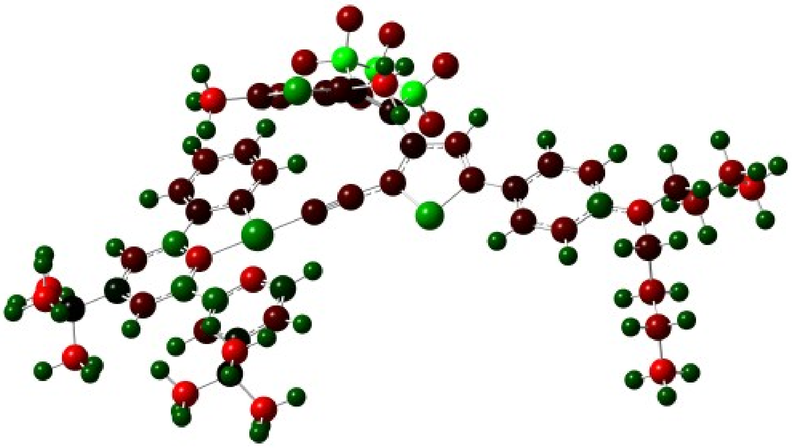


Figure S2. Partial atomic charges based on a NBO population analysis at the PBE0/LANL2DZP level of theory. The atoms are coloured based on their partial charge: red (negative charge) and green (positive charge).

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