

# Synthesis and photophysical characterization of new push-pull oligothiophenes systems.

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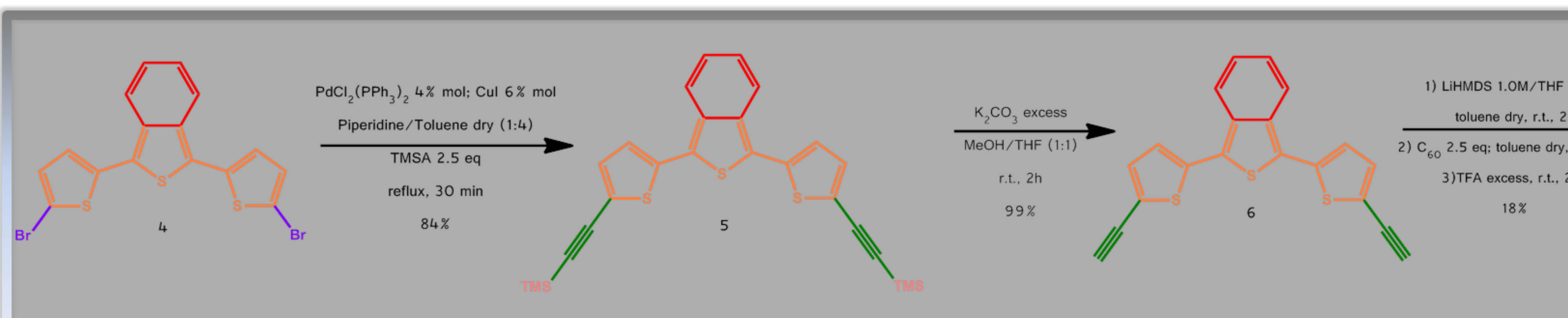
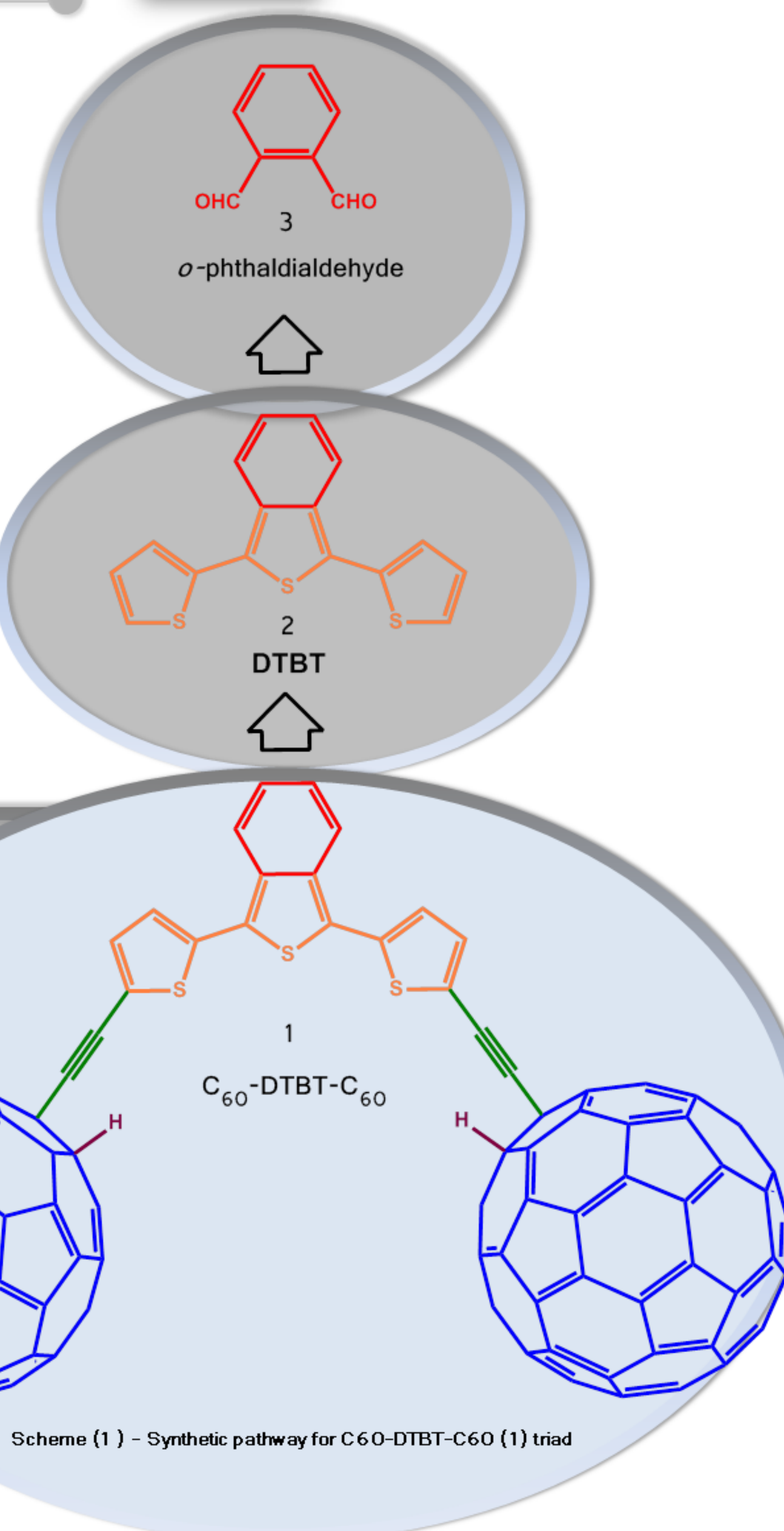
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**Introduction and objectives.** This work aims at synthesizing and then characterizing photophysically new  $\pi$ -conjugated systems designed as fullerene acceptor/oligothiophene donor/fullerene acceptor triad coupled by two ethynyl bridges **1**. Oligothiophenes are an important class of organic semiconductors which in the presence of acceptor groups in  $\alpha$ -positions can behave as push-pull systems showing nonlinear optical properties desirable for optoelectronic applications [1]. Their ability of combining potential advantages such as better photostability and smaller band gap than other conjugated systems, for instance, such as PPV derivatives, have allowed their wide-spreading as the most used substrates for the synthesis of fullerene  $C_{60}$ -derivatized conjugated oligomers. The knowledge of energy and electron transfer processes is relevant in elucidating the working principles of systems of this kind aiming at converting solar energy into electricity. Mimicking natural systems with properly designed synthetic analogues has provided valuable insight on paths followed during charge separation and recombination processes occurring after photoexcitation in donor-acceptor  $\pi$ -conjugated molecules. A large number of studies have shown that both **electronic** (excitation energy and redox potentials) and **structural properties** (distance, orientation, and nature of bridges) are, in molecular systems, critical parameters that control the kinetics of charge transfer processes.

**Synthetic approach.** It has been designed by seven consecutive steps (scheme 1) with an overall 37% yield starting from a commercially available and affordable *o*-phthalaldehyde **3** precursor [2]. The last 3 steps have been set-up for the first time during this work [3]. The best reaction conditions experimentally found are described here after:



**Photophysical characterization.** The Femtosecond Transient Absorption Pump-Probe Spectroscopy (the working principle is shown in figure 2) has been used in order to study the electronic properties of the new synthesized donor-acceptor compound **1**. Pump and probe laser beam pulses have been properly chosen.

## UV-vis and emission spectra.

Considering the figure 3 absorption spectrum the 480 nm laser pump pulse has been employed for exciting the DTBT donor moiety of the triad system **1** under study. The emission spectrum of figure 3 has suggested to select, as the main monitor, the 575 nm probe transmitted beam. The absorption spectrum of C<sub>60</sub>-DTBT-C<sub>60</sub> system in toluene corresponds closely to the linear superposition of the individual spectra, acquired in the same solvent, which can be related to a mixture of both DTBT and C<sub>60</sub> in a 1:2 ratio. Results of figure 4 provide the conclusion that electronic interaction between the donor DTBT and the acceptor C<sub>60</sub> belonging to the triad molecule in the ground state can be excluded.

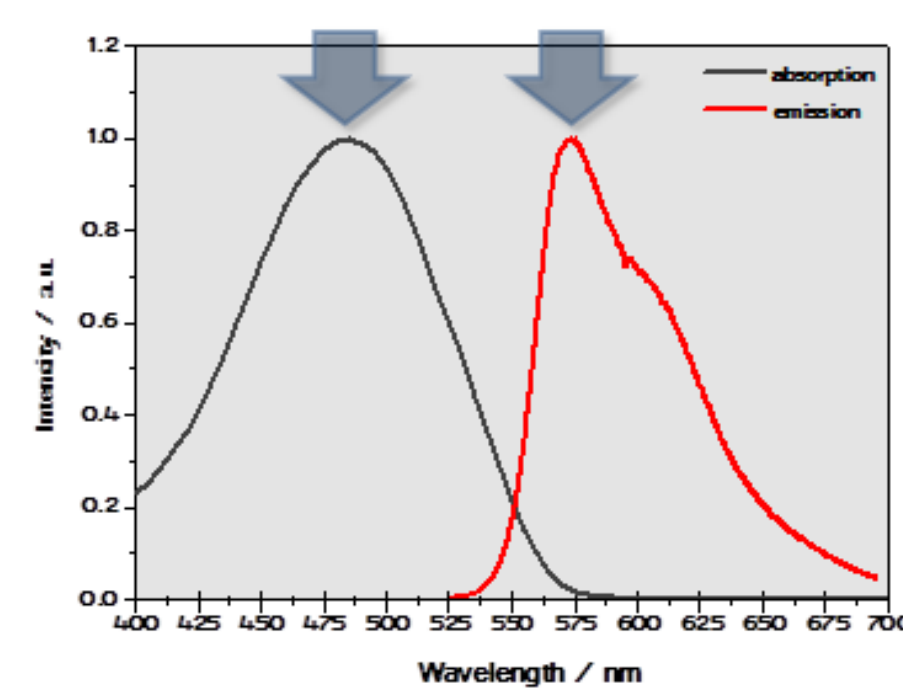


Figure (3) - C<sub>60</sub>-DTBT-C<sub>60</sub> UV-vis absorption and emission spectra of a solution 0.044 mM in CHCl<sub>3</sub> (black) and 0.5 mM in CHCl<sub>3</sub> (red). The emission spectrum has been obtained by pumping the system through a laser beam at  $\lambda = 480$  nm.

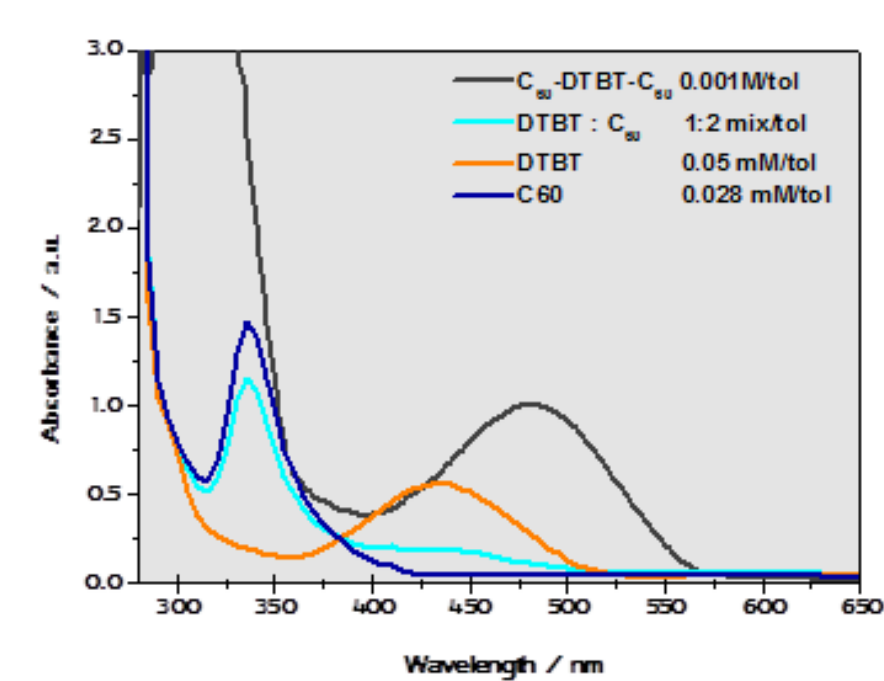


Figure (4) - Toluene solutions UV-vis absorption spectra of: C<sub>60</sub>-DTBT-C<sub>60</sub>, 0.001 M (grey); DTBT, 0.05 mM (orange); C<sub>60</sub>, 0.028 mM (blue); 1:2 ratio of DTBT/C<sub>60</sub> (light blue).

**Conclusions.** During this work a new promising and versatile synthetic approach to compound **1** has been set-up for the first time. On the new compound **1** the use of Transient Pump-Probe Spectroscopy has evidenced the path followed when photoinduced intramolecular charge transfer from the donor moiety (DTBT) to the acceptor counterpart (C<sub>60</sub>) of C<sub>60</sub>-DTBT-C<sub>60</sub> takes place. Furthermore, by DFT/B3LYP/6-31G+(d,p) theoretical calculations showing that the involved is HOMO  $\rightarrow$  LUMO transition is caused by an electron-transfer process [2], this hypothesis is even confirmed.

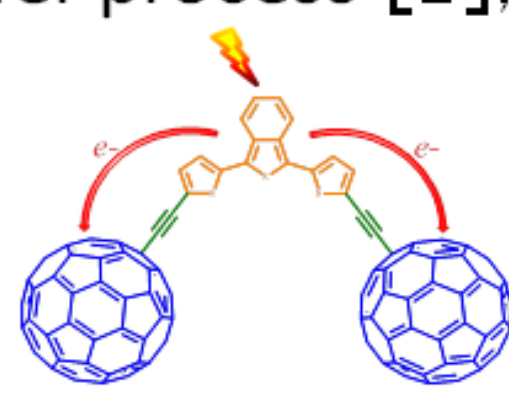


Figure (9) - HOMO and LUMO of C<sub>60</sub>-DTBT-C<sub>60</sub>. The HOMO is found at -0.17177 eV and it is mainly localized on the DTBT part of the molecule; while the LUMO is found at 0.11032 eV and localized on the fullerene

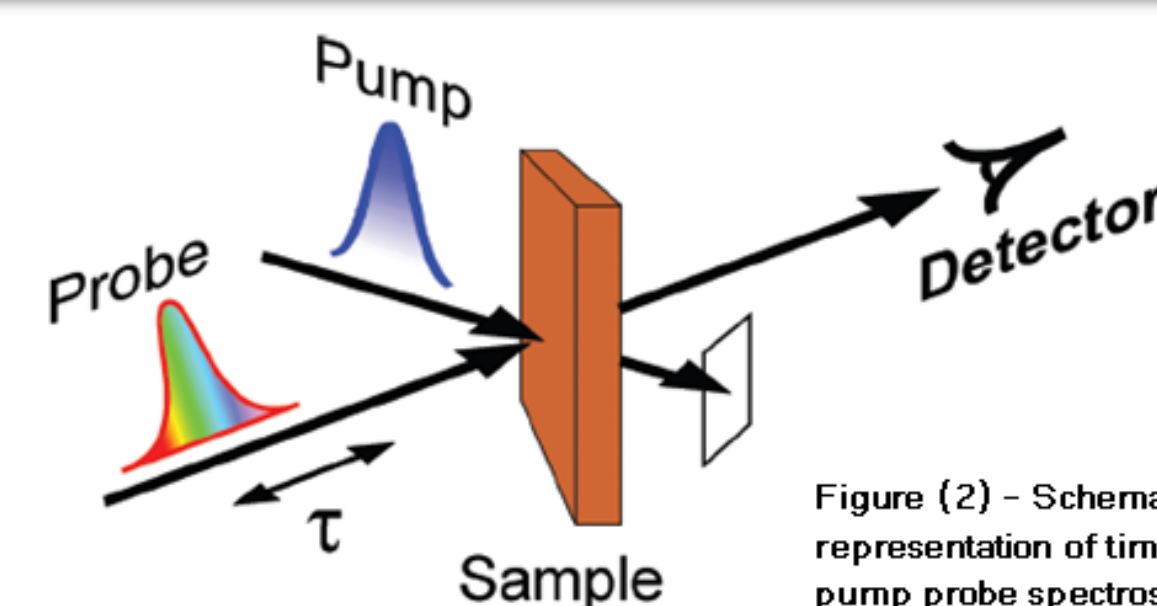


Figure (2) - Schematic representation of time-resolved pump-probe spectroscopy

**Pump-probe spectra and results.** The electronic properties change deeply depending on the solvent polarity. Acquisition of pump-probe spectra in two different solvents has been performed:

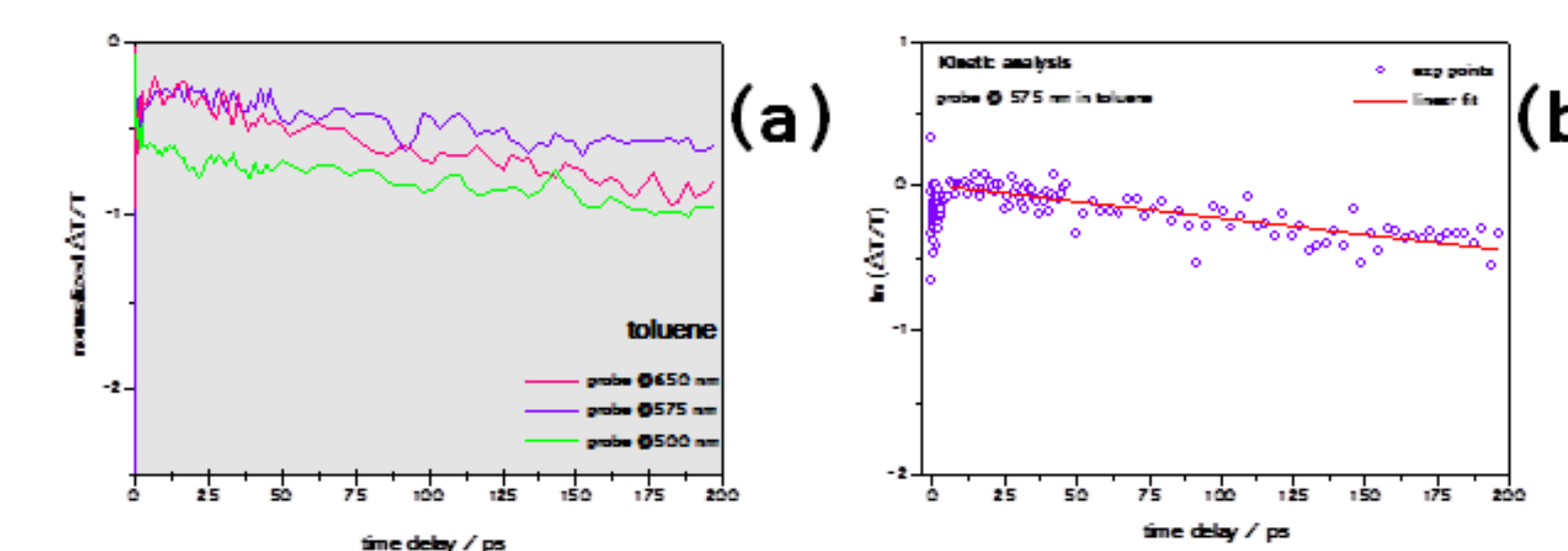


Figure (5) - (a) Pump-probe spectrum of C<sub>60</sub>-DTBT-C<sub>60</sub> 1x10<sup>-3</sup>M solution in toluene excited by a pump pulse of 480 nm. (b) Kinetic analysis related to p-p data acquired @575nm as probe beam.

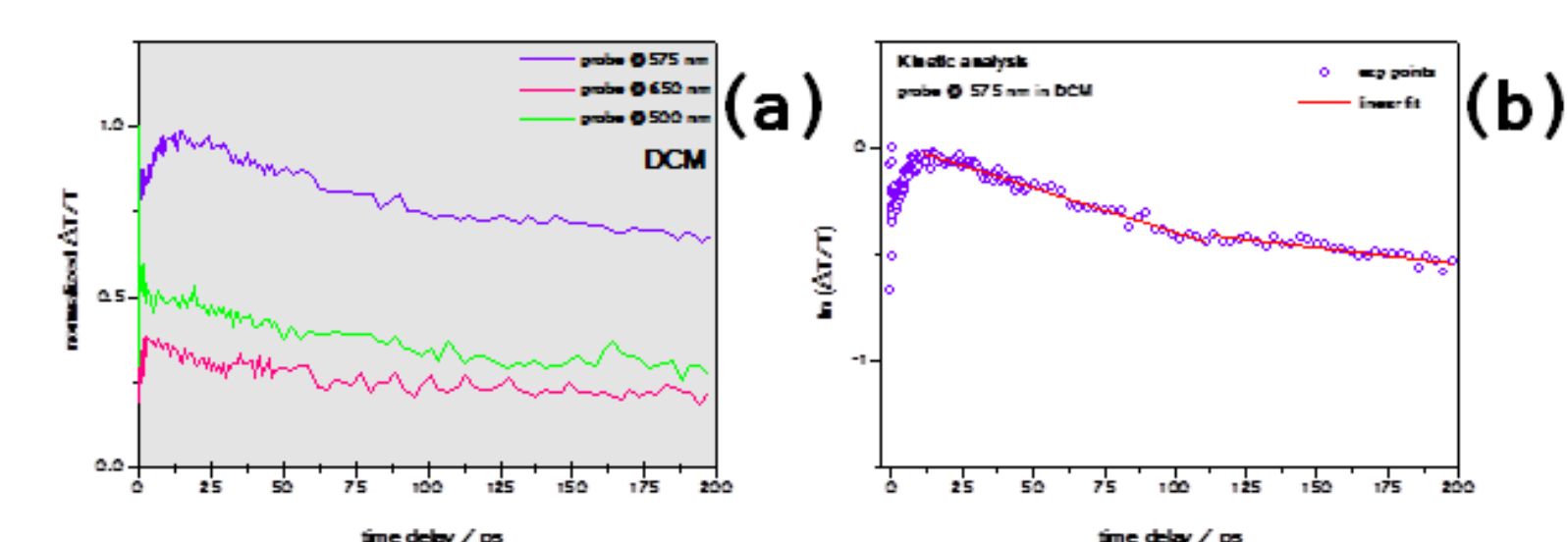


Figure (6) - (a) Pump-probe spectrum of C<sub>60</sub>-DTBT-C<sub>60</sub> 1x10<sup>-3</sup>M solution in DCM excited by a pump pulse of 480 nm. (b) Kinetic analysis related to p-p data acquired @575nm as probe beam.

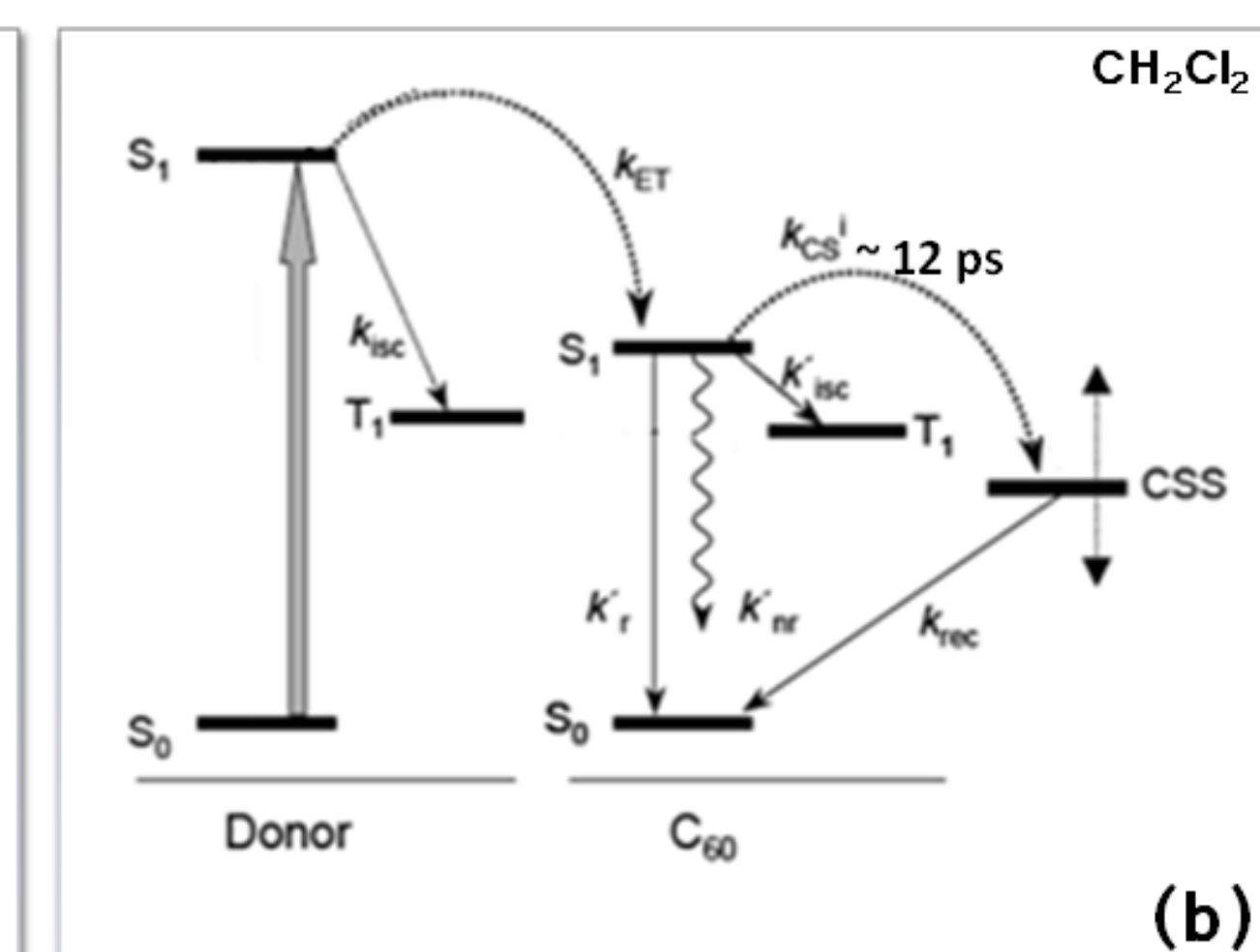
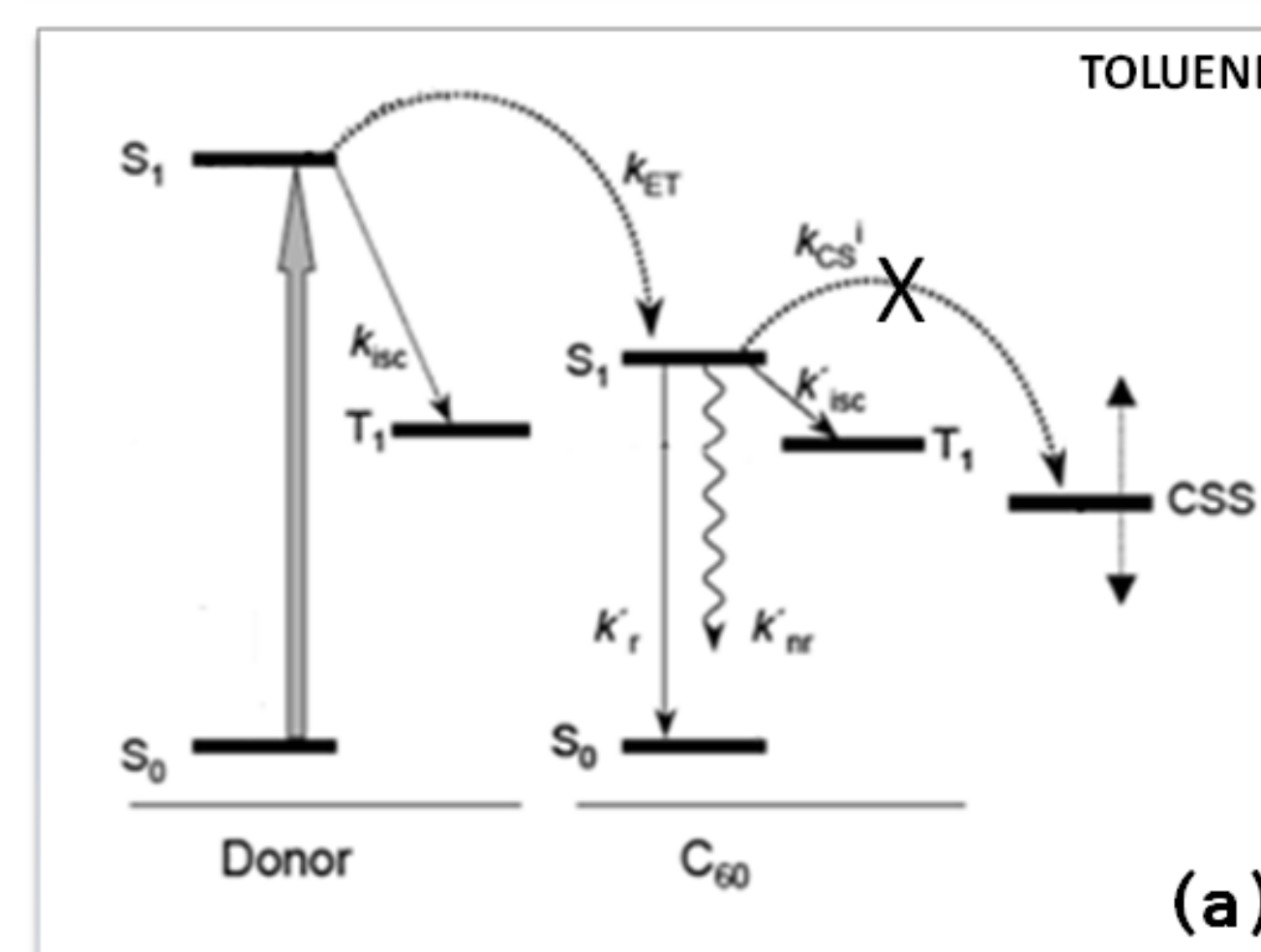
A different behavior could be evidenced in figure 5(a) and 6(a). Comparing kinetic data of C<sub>60</sub>-DTBT-C<sub>60</sub> solutions in different solvents @575 nm (fig. 5(b),6(b) and table 7) we deem that an electron transfer could occur leading to the charge separated DTBT<sup>+</sup>(C<sub>60</sub><sup>-</sup>)<sub>2</sub> state (CSS).

Toluene ( $\epsilon = 2.38$ )  $\rightarrow$  after the formation of C<sub>60</sub>(S<sub>1</sub>) excited state by ultrafast energy transfer process it follows a relaxation initially by ISC and then via fluorescence T<sub>1</sub>  $\rightarrow$  S<sub>0</sub>.

CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon = 8.93$ )  $\rightarrow$  formation of CSS in 12 ps could be correlated with a direct electron transfer process (K<sub>CS</sub><sup>i</sup>) (generally it takes less than 18 ps in similar systems [4]).

C <sub>60</sub> -DTBT-C <sub>60</sub>	TOLUENE		CH <sub>2</sub> Cl <sub>2</sub>	
Experimental p-p kinetic data	relaxation time	kinetic constant	relaxation time	kinetic constant
Probe @ 575 nm	$\tau_{ISC} = 434.8 \pm 27.1$ ps	$k_{ISC} = 2.30 \times 10^9$ s <sup>-1</sup>	$\tau_{ET} = 24.0 \pm 5.7$ ps $\tau_{CS} = 64.0 \pm 61.9$ ps	$k_{ET} = 4.16 \times 10^9$ s <sup>-1</sup> $k_{CS}^i = 1.56 \times 10^9$ s <sup>-1</sup>

Table (7) - Experimental pump-probe kinetic data related in turn to TOLUENE and DCM solutions of C<sub>60</sub>-DTBT-C<sub>60</sub>. The 575nm wavelength has been employed as the transmitted probe pulse.



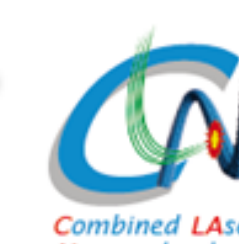
Scheme (8) - Schematic diagram describing the energy level of the singlet (S<sub>1</sub> $\rightarrow$ S<sub>0</sub>) and charge-separated (CSS) state of C<sub>60</sub>-DTBT-C<sub>60</sub> triad in both toluene (a) and in CH<sub>2</sub>Cl<sub>2</sub> (b). The energy transfer (K<sub>ET</sub>) and the indirect charge separation paths are indicated with the curved dotted arrows together with the natural decays of both chromophores (thin solid arrows). The thick grey arrow describes the initial excitation of the DTBT moiety.

## References

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