Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Diacetylene Bridged Triphenylamines as Hole Transport Materials for Solid State Dye Sensitized Solar Cells

Miquel Planells,[a‡] Antonio Abate,[b‡] Derek J. Hollman,[b] Vishal Bharti,[c] Jitender Gaur,[c] Dibyajyoti Mohanty[c], Suresh Chand,[c] Henry J. Snaith[b] and Neil Robertson[a]

[a]EastChem – School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

[b]Department of Physics, University of Oxford, Oxford OX1 3PU, U.K.

[c]CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi-110012, India

[‡] These authors contributed equally.

TABLE OF CONTENTS

Supporting Information Figures

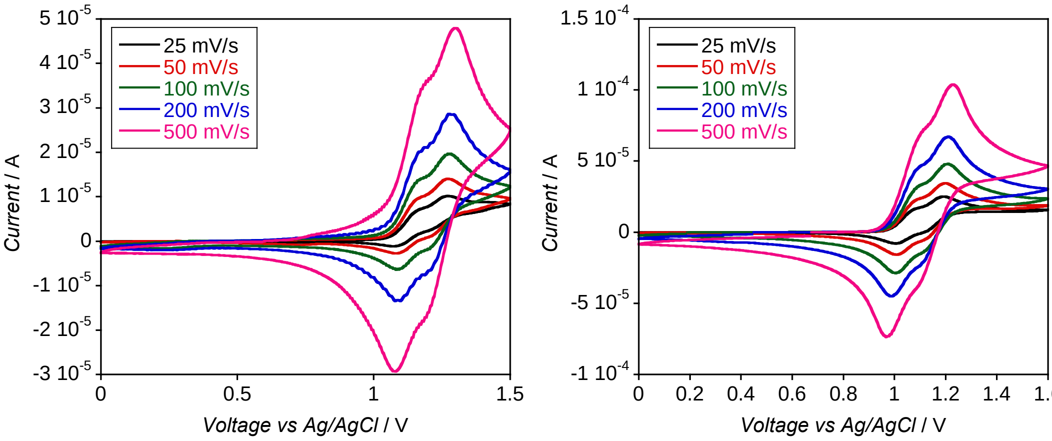


Figure S1. Cyclic voltammetry traces at different scan rates of **H-DATPA** (*left*) and **Me-DATPA** (*right*).

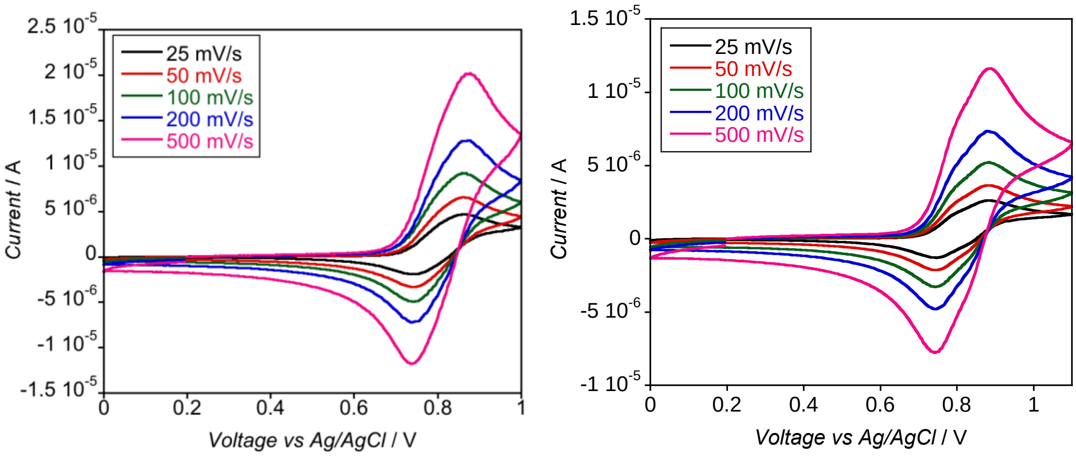


Figure S2. Cyclic voltammetry traces at different scan rates of **MeS-DATPA** (*left*) and **MeO-DATPA** (*right*). Note that the two-oxidation process can barely be observed, and therefore, pulse voltammetry techniques must be used.

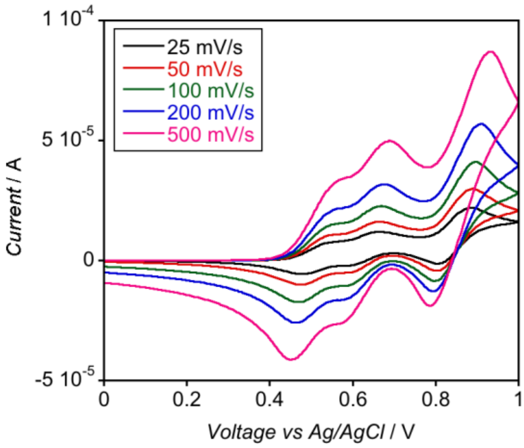


Figure S3. Cyclic voltammetry traces at different scan rates of Spiro-OMeTAD.

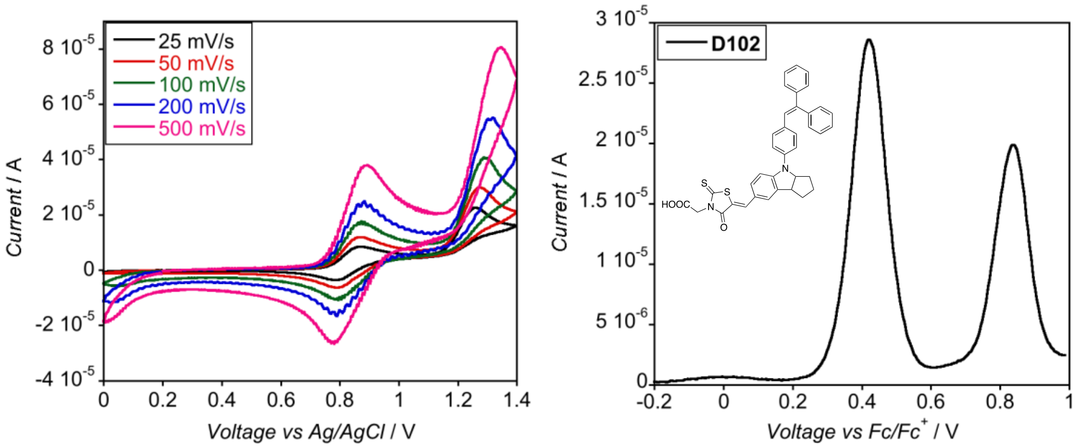


Figure S4. Cyclic voltammetry at different scan rates (*left*) and square-wave voltammetry (*right*) traces of **D102** dye in CH_2Cl_2 solution.

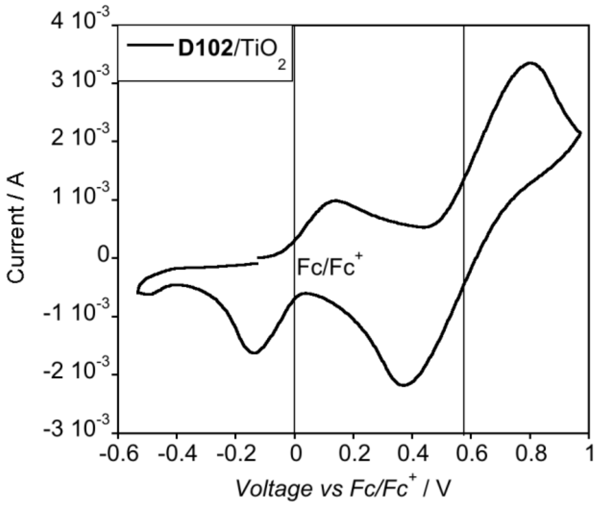


Figure S5. Cyclic voltammetry of **D102** anchored onto mesoporous TiO_2 nanoparticles. Square-wave voltammetry could not be measured due to high intense signal.

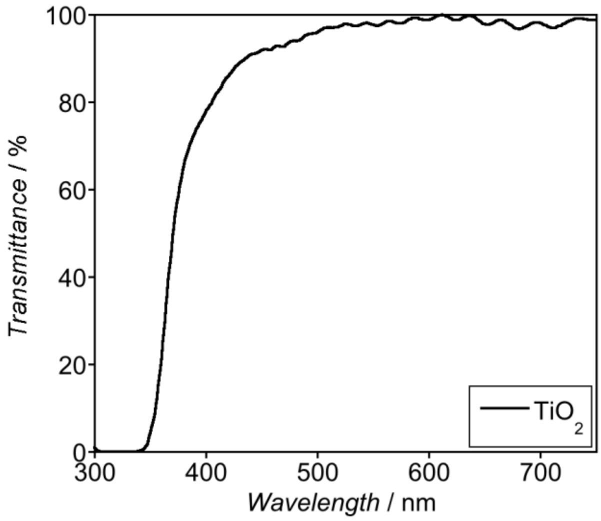


Figure S6. Transmittance of TiO_2 mesoporous film.

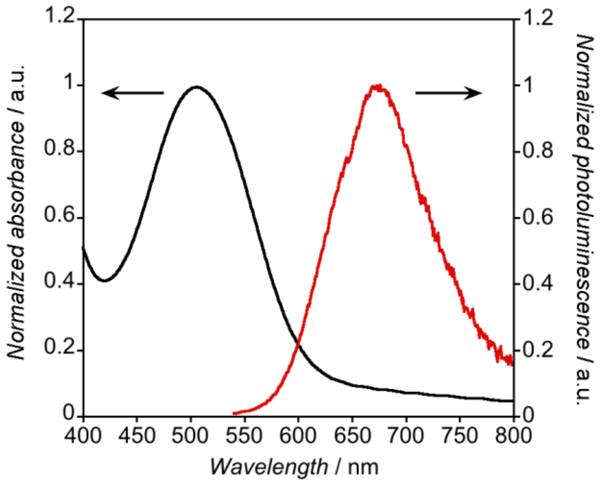


Figure S7. Absorption (*black line*) and emission (*red line*) spectra of **D102** anchored onto mesoporous TiO_2 nanoparticles.

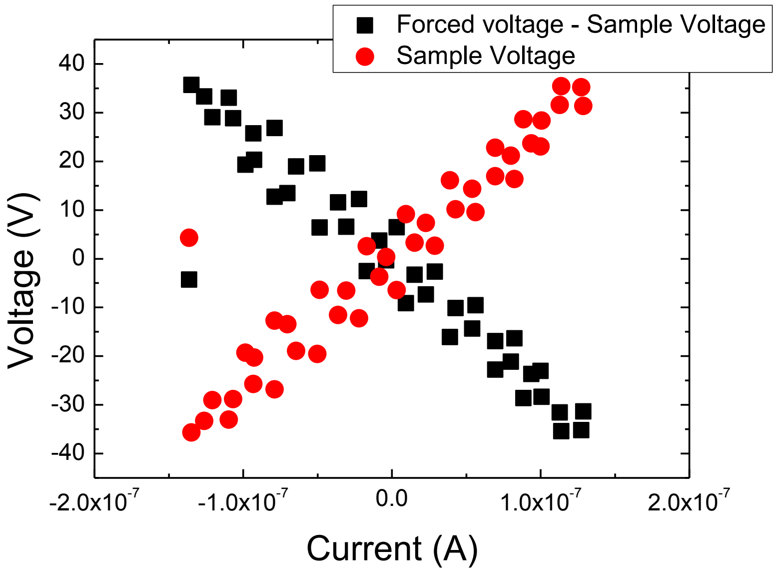


Figure S8. Four point conductivity measurements for Spiro-OMeTAD (with and without LiTFSI) have been used to estimate the contact resistance according to the previous report *J. Appl. Phys.* **2004**, *96*, 7312.

Supporting Information Tables

Table S1. HOMO energies of DATPA derivatives obtained by DFT calculations performed at B3LYP/6-31G(d) level of theory *versus* experimental values from electrochemical measurements.

	DFT (*gas phase*)	**DFT** (CH_2Cl_2)	**Experimental**
H-DATPA	-4.75 eV	-4.92 eV	-5.33 eV
Me-DATPA	-4.63 eV	-4.83 eV	-5.23 eV
MeS-DATPA	-4.61 eV	-4.77 eV	-5.14 eV
MeO-DATPA	-4.52 eV	-4.69 eV	-5.02 eV

Table S2. Charge transport parameters in the samples generated by theoretical fitting of experimental curves reported in the main text. Carrier mobility μ, effective density of states N_V, total trap density H_b and characteristic trap energy E_t.

	μ ($cm^2V^{-1}s^{-1}$)	N_V (cm^{-3})	H_b (cm^{-3})	E_t (meV)
H-DATPA	3.0×10^{-6}	1×10^{19}	5.5×10^{18}	40
Me-DATPA	2.8×10^{-6}	1×10^{19}	6.0×10^{18}	51
MeS-DATPA	4.0×10^{-6}	1×10^{19}	1.6×10^{18}	91
MeO-DATPA	6.0×10^{-6}	1×10^{19}	7.0×10^{17}	88
Spiro-OMeTAD	3.6×10^{-4}	1×10^{19}	4.0×10^{18}	32

Detailed description of mobility measurements

Earlier studies in organics have shown that the space-charge limited current (SCLC) governs the charge transport either by drift of charge carriers under the influence of traps, distributed in energy and space-called trap model or by temperature and field dependent mobility models. Due to the low mobility of charge carriers in organic semiconductors, the injected carrier forms a space charge. This space charge creates a field that opposes the applied bias and thus decreases the voltage drop across junction; as a result SCLC have been proposed as the dominant conduction mechanism in organic semiconductors. Ohmic conduction at low fields can be described by:

$$J = qn\mu \frac{V}{d} \tag{1}$$

where, q is the electronic charge, n is the carrier density, μ is the carrier mobility, d is the thickness of the film.

SCLC theory with an exponential trap distribution proposes that the space charge that limits conduction is stored in the traps. Assuming that the trapped carrier density (p_t) >> free carrier density (p) and using continuity equation and boundary condition for current density (J) and applied voltage (V) as:

$$J = q\mu p(x)F(x) \tag{2}$$

$$V = \int F(x)\,dx \tag{3}$$

the expression for J, for traps (N_t) distributed exponentially in energy (E) as:

$$N_t(E) = \left(\frac{H_b}{E_t}\right) e^{\left(-E/E_t\right)} \tag{4}$$

is given by:

$$J = q^{1-l}\mu N_v \left(\frac{2l+1}{l+1}\right)^{l+1} \left(\frac{l\varepsilon\varepsilon_0}{(l+1)H_b}\right)^{l} \frac{V^{l+1}}{d^{2l+1}} \tag{5}$$

where N_V is the effective density of states, ε is the dielectric constant of material, ε_0 is the permittivity of the free space, $N(E)$ is the distribution function of hole trap density at an energy level E above the valence band edge, H_b is the total trap density at the edge of valence band, E_t is the characteristic trap energy that is often expressed in terms of the characteristic temperature of trap distribution T_C as:

$$E_t = k_B T_C \tag{6}$$

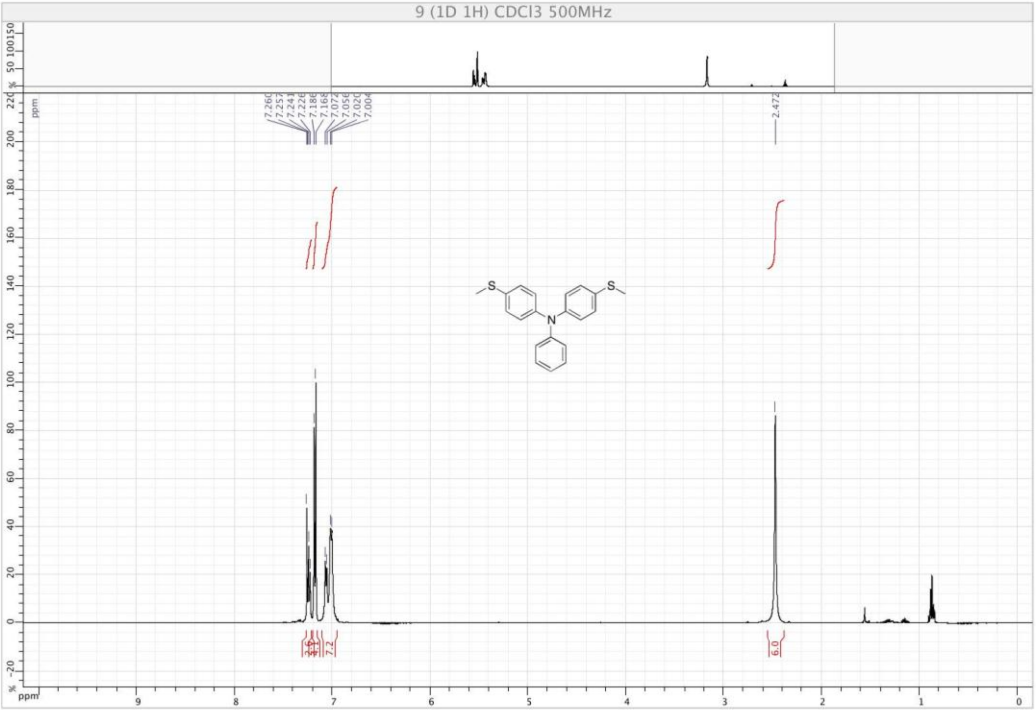
$$l = \frac{E_t}{k_B} = \frac{T_C}{T} \tag{7}$$

where k_B is the Boltzmann constant and the parameter l determines the distribution of traps in the forbidden gap.

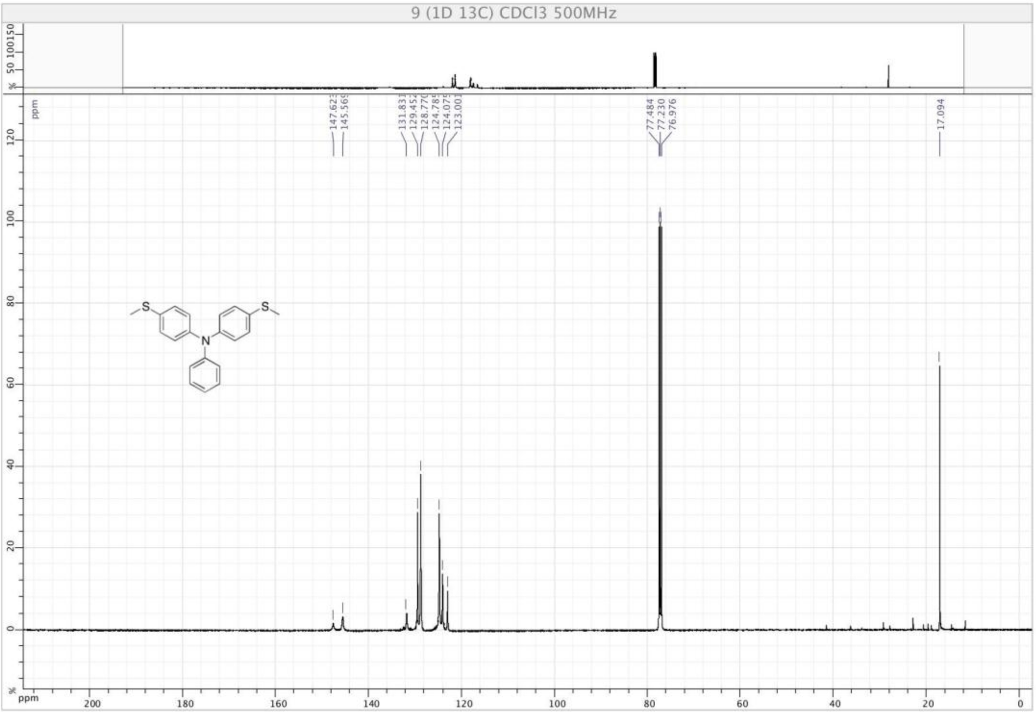
The experimental data has been analyzed in terms of SCLC by generating theoretical curves using equation 5. The theoretical curves generated have been found to fit quite well the experimental data establishing explicitly that the charge transport in all the four samples is governed by trap limited SCLC where traps are distributed in energy and space.

^{1}H and ^{13}C NMR spectra

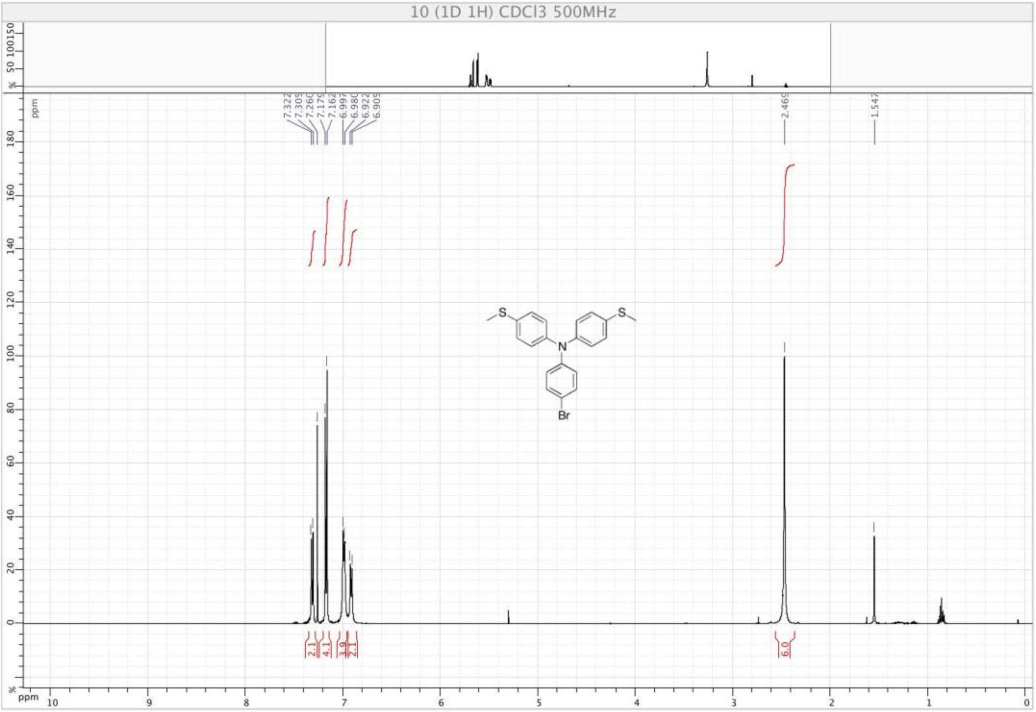
^{1}H-NMR of **9**



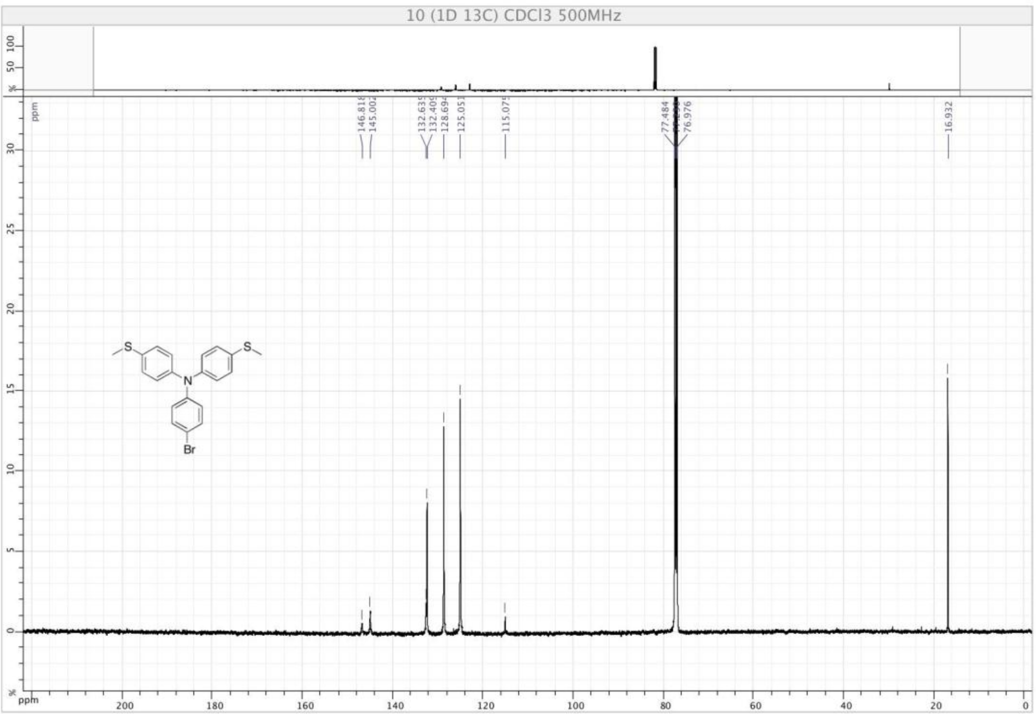
^{13}C-NMR of **9**



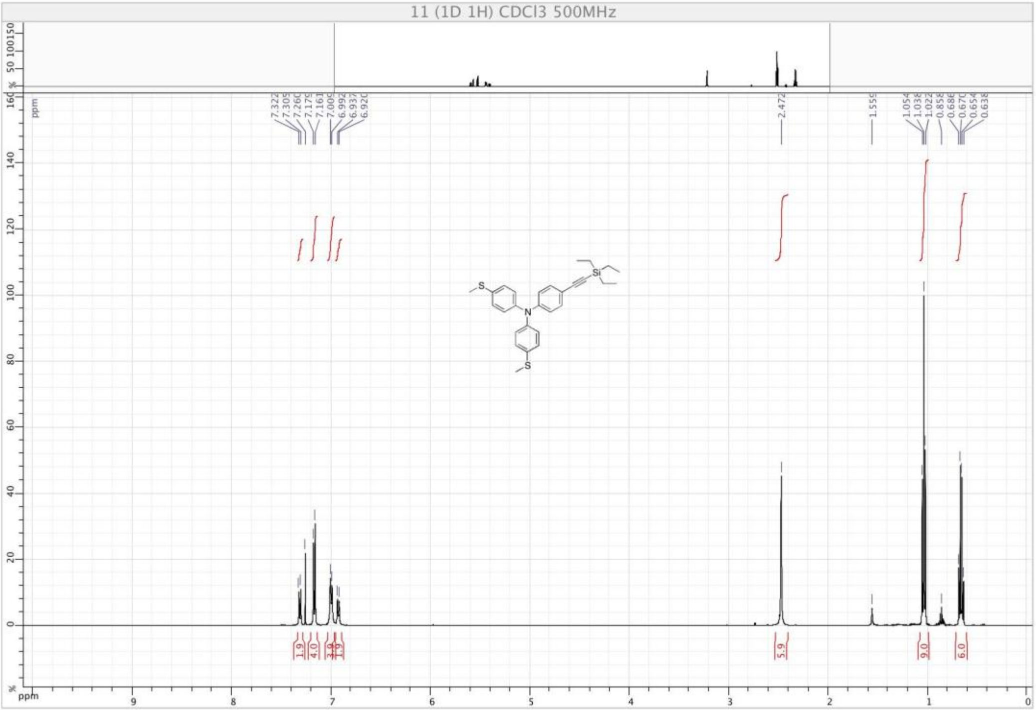
^{1}H-NMR of **10**



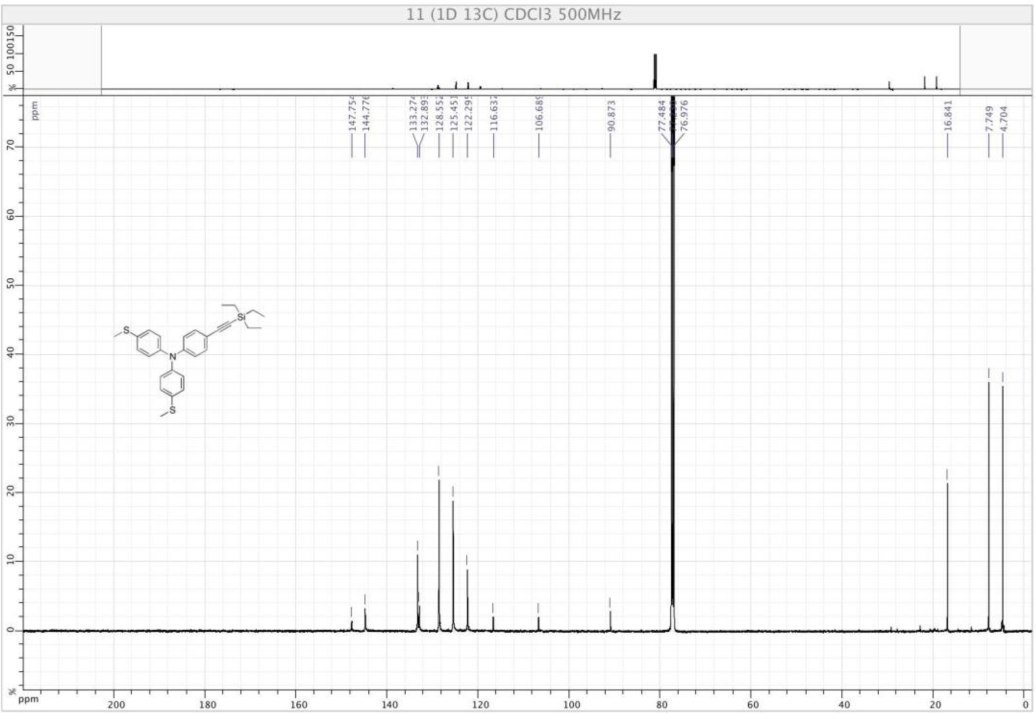
^{13}C-NMR of **10**



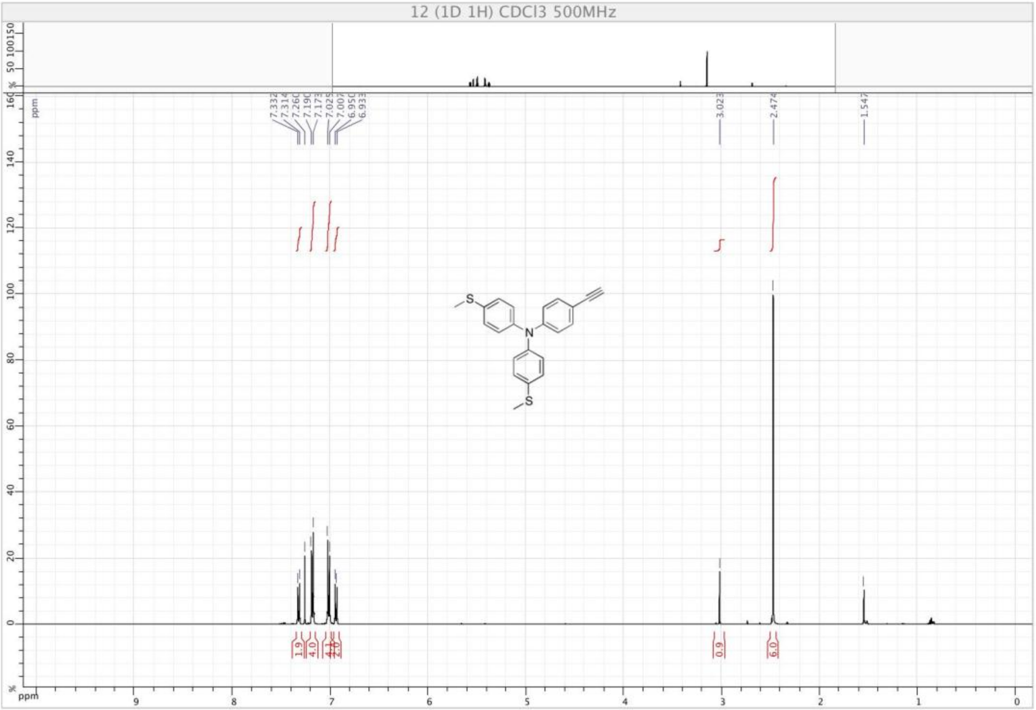
^{1}H-NMR of **11**



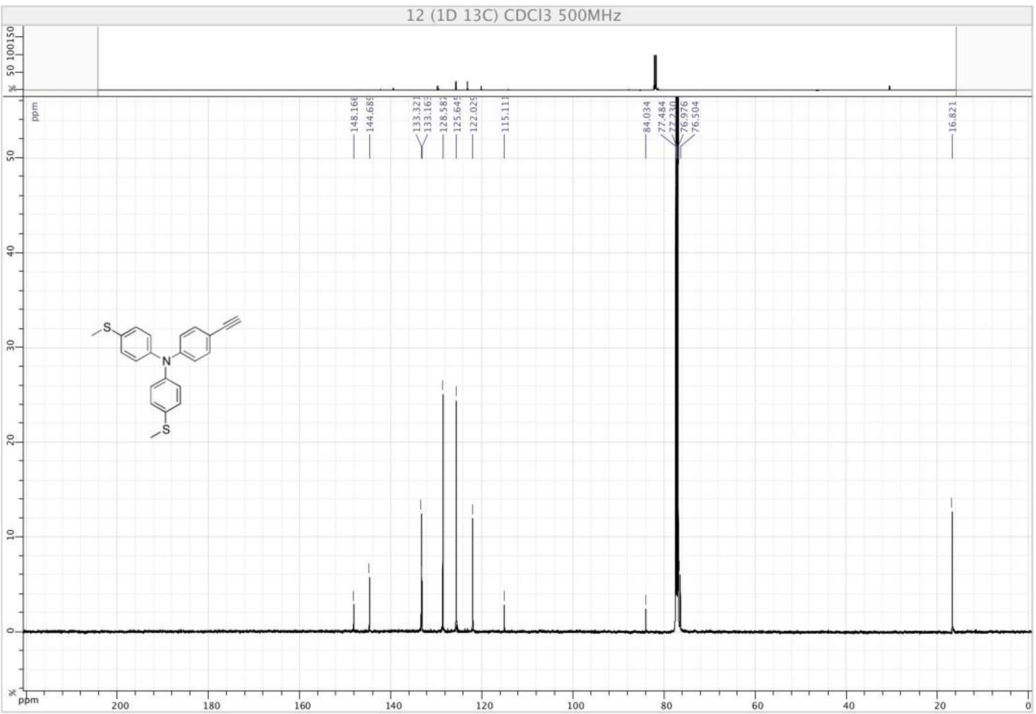
^{13}C-NMR of **11**



^{1}H-NMR of **12**



^{13}C-NMR of **12**



Fluorescence lifetime of D102 on Al2O3 in absence of any of the hole conductors