# Supporting Information

## Charge Transfer Liquid: A Stable Donor-Acceptor Interaction in Solvent-free Liquid State

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**Content**

# Experimental

## Materials

All chemicals, 12-tricosanone, 1-bromo-2-ethylhexane, 1,8-naphthalic anhydride, naphthalene-1,4,5,8-tetracarboxylic dianhydride (TCI), 2-ethylhexyl amine, ammonium acetate (Spectrochem), sodium cyanoborohydride, dithranol (Aldrich), 2,6-dihydroxynaphthalene (Alfa Aeser) and hydrochloric acid (Spectrochem) were used as received. The solvents such as dichloromethane, methanol, dimethylformamide (Finar) were used as received without further purification. Thin layer chromatography was carried out using Aluchrosep Silica Gel 60/UV254 purchased from Merck Specialities Pvt Ltd and visualized either by UV Fluorescence or by iodine chamber. Column chromatography was performed using silica gel (100-200 mesh), bed was made by using 60-120 mesh silica purchased from Spectrochem Pvt. Ltd. India and mixtures of dichloromethane-PET used for elution were distilled before use.

## General

All the reactions were carried out in oven dried round bottom flasks under argon atmosphere unless otherwise mentioned. The $^{1}H$, $^{13}C$ NMR spectra were recorded on a Bruker-400 MHz NMR spectrometer. NOESY and ROESY NMR experiments were carried out on a Bruker 700 MHz spectrometer while diffusion experiments were carried out on a Bruker 500 MHz spectrometer equipped with a broad band diffusion probe (DIFF60) generating a maximum gradient of 1700 Gauss/cm. The chemical shift values for $^{1}H$ (TMS as internal standard) and $^{13}C$ NMR are recorded in $CDCl_3$. The value of coupling constant (*J*) is stated in Hertz (Hz). MALDI-TOF MS spectrum was recorded using dithranol as the inert matrix on AB SCIEX MALDI TOF/TOF™ 5800. FT-IR spectra were recorded using Bruker Alpha FT-IR spectrometer and reported in frequency of absorption ($cm^{-1}$). UV-Vis absorption spectra were recorded with a Shimadzu 1800 spectrophotometer, while all emission spectra were performed using PTI Quanta Master™ Steady State Spectrofluorometer. The Powder X-ray diffraction patterns were recorded on a Rigaku, MicroMax-007HF equipped with high intensity Micro focus rotating anode X-ray generator. The data was collected with the help of Control Win software. A Rigaku, R-axis IV++ detector was used for the wide-angle experiments using Cu K (1.54 Å) radiation outfitted with a Ni filter and Aluminium holder was used as sample holder. DSC Q 10 differential scanning calorimeter connected to Q Series

PCA (TA Instruments, USA) was used to determine the phase transition temperatures of molecule. TGA data was collected in METTLER TOLEDO, TGA/SDTA851 instrument. Rheology experiment was carried out using a MCR dynamic oscillatory Cup and Bob Frequency Sweep at 20 $^{o}$C by using about 5 g of the liquid samples.

**Preparation of liquid CT complex**

The donor 1 and acceptor 2 with different equivalents in glass vials (1.5 mL) were either stirred well with spatula or heated gently to become a homogeneous mixture.

**UV-VIS spectrum of neat liquids**

UV-Vis spectra of all neat liquids were recorded in the transmittance mode and the samples are prepared by making a uniform transparent coating of 5 mg sample on 1 x 1 $cm^2$ area of quartz plate. The consistency of each spectrum was confirmed by repeated trails.

**NMR experiments**

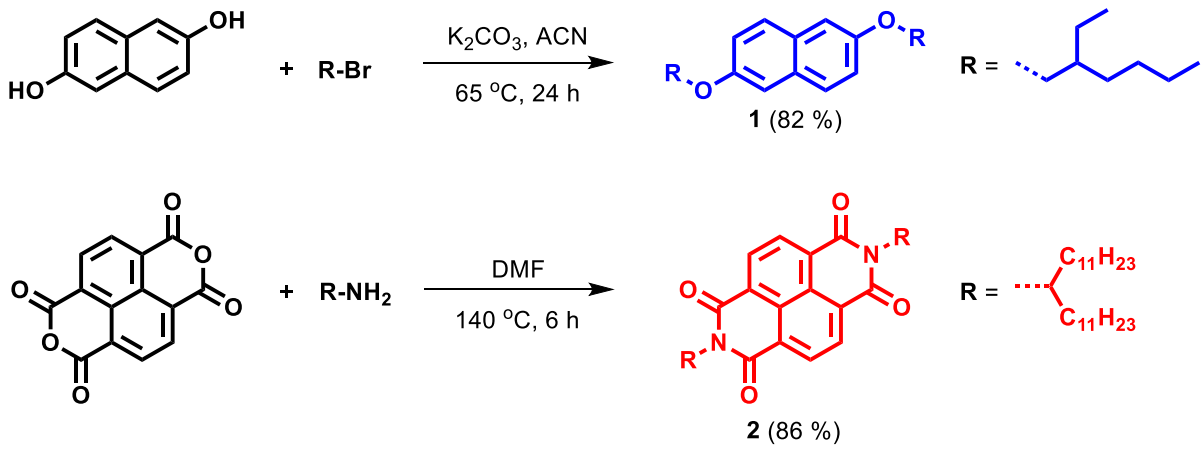
NMR spectra in *n*-hexane were recorded using DMSO-$d_6$ as the external reference. All the NMR spectra in the neat condition (1, 2 and 1+2 CT liquids) were recorded by placing the compounds (~ 200 mg) in a 3 mm NMR tube and inserting it in an outer 5 mm NMR tube containing DMSO-$d_6$ as an external lock. After mixing, samples were allowed to homogenize at the measurement temperature before carrying out the experiments. The actual ratios of **1** and **2** were estimated by integration of peak areas of the aromatic protons.

**Molecular dynamics (md) simulations**

All MD simulations were performed using Gromacs 5.0.7 software. Molecule **3** with short branched alkyl chain has been chosen for facile MD simulations. The GAFF force field parameters for compound **1** and **3** were generated using the antechamber utility of AmberTools 18. A cubic simulation box containing 10 acceptor and 100 donor molecules (D:A = 1:0.1) was prepared with periodic boundary conditions. The system was energy minimized using steepest descent algorithm. All the systems were equilibrated for 2 ns in NPT ensemble using a velocity rescale thermostat and Parrinello-Rahman barostat at 300 K and 1 bar. Long-range electrostatic interactions were calculated with the particle mesh Ewald (PME) summation method with a grid spacing of 0.16 nm and fourth-order cubic interpolation. For short range electrostatics and van der Waals interaction, a cut-off distance of 1 nm was used. The integration time step was set to 2 fs. The production run was further continued for 100 ns and coordinates were saved every 20 ps for further analysis. Radial distribution functions (RDF) captures the statistical distribution of the distance between chosen pairs.

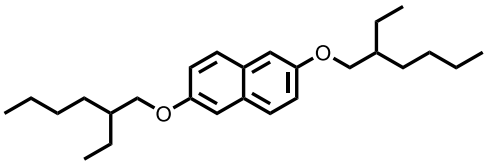
## Synthesis

Molecules**1** and **2** are synthesized as shown in Scheme S1.




**Scheme S1.** Synthesis of **1**and **2**.

## Procedure for synthesis of 2,6-bis((2-ethylhexyl)oxy)naphthalene[S1]



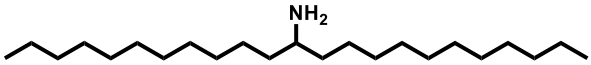

Potassium carbonate 8.6 g (5 eq.) was suspended in 50 ml of acetonitrile and sonicated for 30 min followed by degassing $N_2$ for 30 minutes. 12 g (5 eq.) of 2-ethylhexyl bromide was added into above reaction mixture. Separately 2 g (1 eq.) of 1,5-dihydroxynaphthalene suspended in acetonitrile and added via a dropping funnel to the reaction mixture. After completion of addition, the reaction mixture was refluxed under $N_2$ for 24 h. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was filtered, the filtrate collected and solvent removed under reduced pressure. The residue obtained was dissolved in chloroform and washed with 1M hydrochloric acid, water and brine. The organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography by using 10% dichloromethane in petroleum ether as an eluent ($R_f$ = 0.8). Combined organic layer was concentrated under reduced pressure and dried under vacuo to yield a colourless liquid (3.94 g, 82%).

**$^{1}$H-NMR** (400 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 7.63 (2H, d, *J* = 8.7 Hz), 7.14-7.12 (2H, dd, *J* = 8.7 and 2.26 Hz), 7.10 (2H, d, *J* = 2.26 Hz), 3.95-3.93 (4H, m), 1.79 (2H, m), 1.55-1.38 (8H, m), 1.37-1.34 (8H, m), 0.98-0.91 (12H, m) ppm.

**$^{13}$C-NMR** (100 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 155.76, 129.66, 127.91, 119.24, 106.88, 70.55, 39.41, 30.60, 29.11, 23.94, 23.06, 22.9, 14.09, 11.14 ppm.

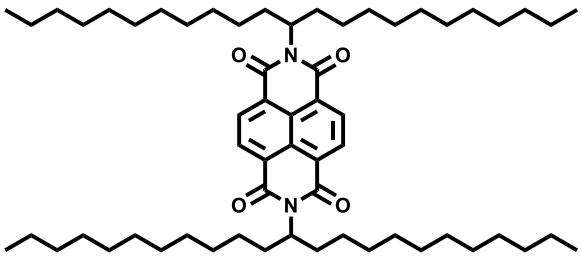
**MALDI-TOF MS**: calcd. for $C_{26}H_{40}O_2$ = 384.6040, found 384.2239.

**Tricosan-12-amine**[S2]




1,2-Tricosanone, ammonium acetate ($NH_4OAc$) and sodium cyanoborohydride ($NaBH_3CN$) were dissolved in 40 ml methanol (HPLC grade) and stirred at RT for 56 h (3 days). After a clear solution was observed in the reaction mixture, it was quenched by adding conc. hydrochloric acid dropwise. The solution was then concentrated with rotatory evaporator. The solid thus obtained was dispersed in 250 ml of water and adjusted to pH = 10 with KOH. The obtained latex solution was extracted by using 150 ml of dichloromethane two times. Combined organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure to give pale yellow liquid in quantitative yield. The amine obtained was used further without purification.

**2,7-di(tricosan-12-yl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone**[S3]



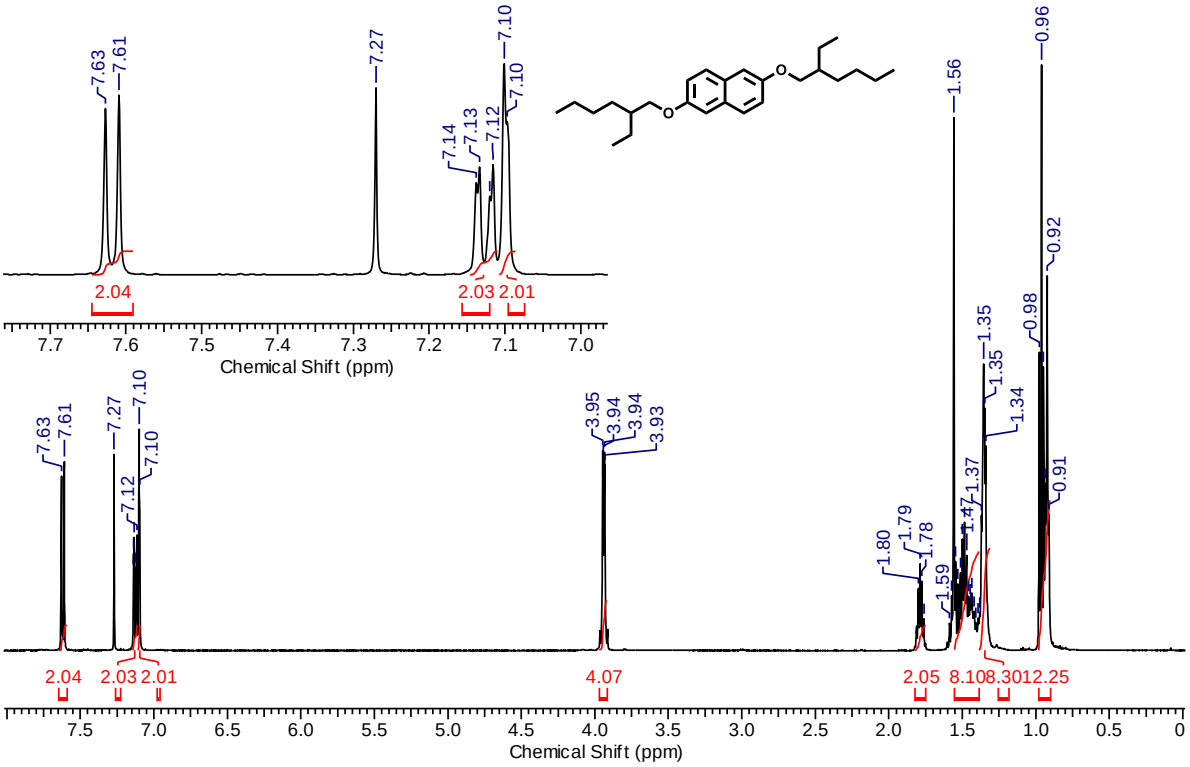

Naphthalene-1,4,5,8-tetracarboxylic dianhydride (200 mg, 1 eq.) and tricosan-12-amine (633 mg, 2.5 eq.) were suspended in DMF (20 mL) in 100 ml round bottom flask. The reaction mixture was stirred for 6 h at 140°C. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to RT and it was quenched by addition of hydrochloric acid (2N, 40 mL). Reaction mixture was extracted with dichloromethane (3 × 200 mL). The organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by silica gel

column chromatography by using 50% dichloromethane in petroleum ether as an eluent ($R_f$ = 0.6). Combined organic layer was concentrated under reduced pressure and dried under vacuo to yield a light brown colour solid (584 mg, 86%).

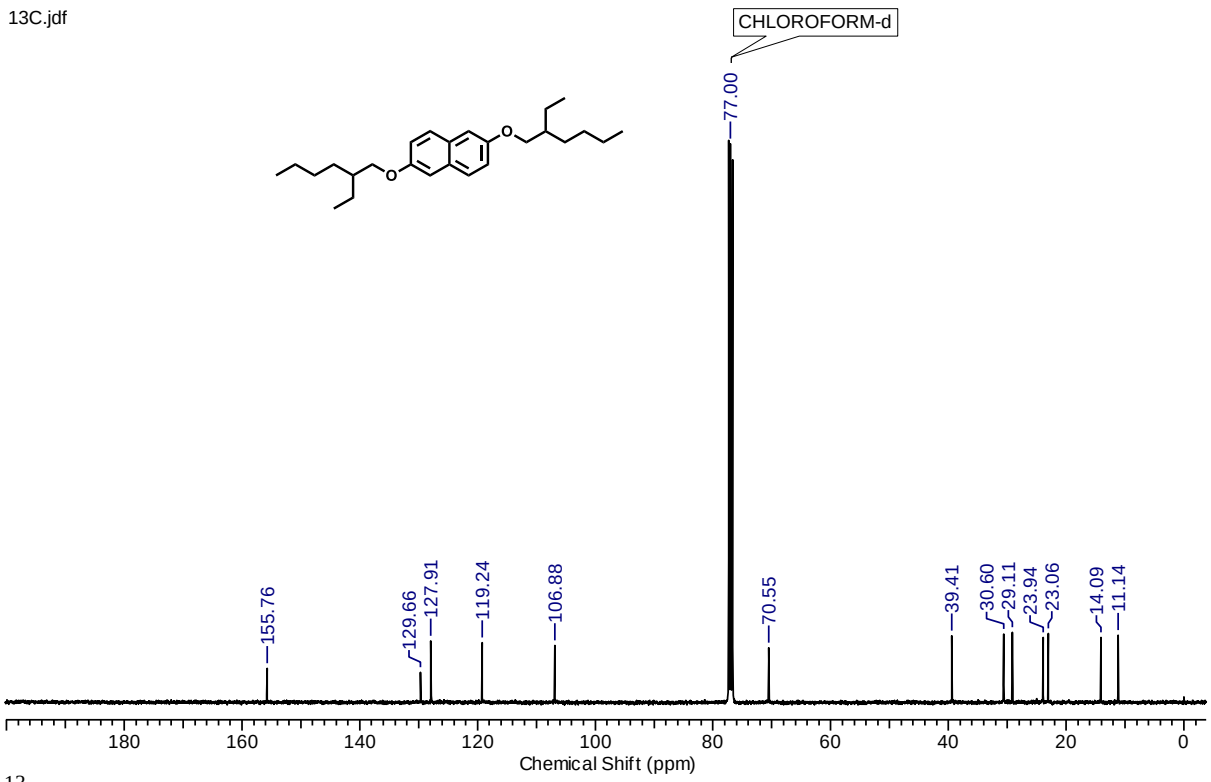
**$^1$H-NMR** (500 MHz, $CDCl_3$, 25 $^oC$): $\delta$ = 8.73 (4H, s), 5.21-5.12 (2H, m), 2.24-2.17 (4H, m), 1.87-1.78 (4H, m), 1.33-1.19 (72H, m), 0.85 (12H, t, $J$ = 6.8 Hz) ppm.

**$^{13}$C-NMR** (125 MHz, $CDCl_3$, 25 $^oC$): $\delta$ = 164.1, 162.9, 131.3, 130.6, 126.8, 55.2, 32.3, 31.9, 29.6, 29.5, 29.3, 26.9, 22.7, 14.1 ppm.

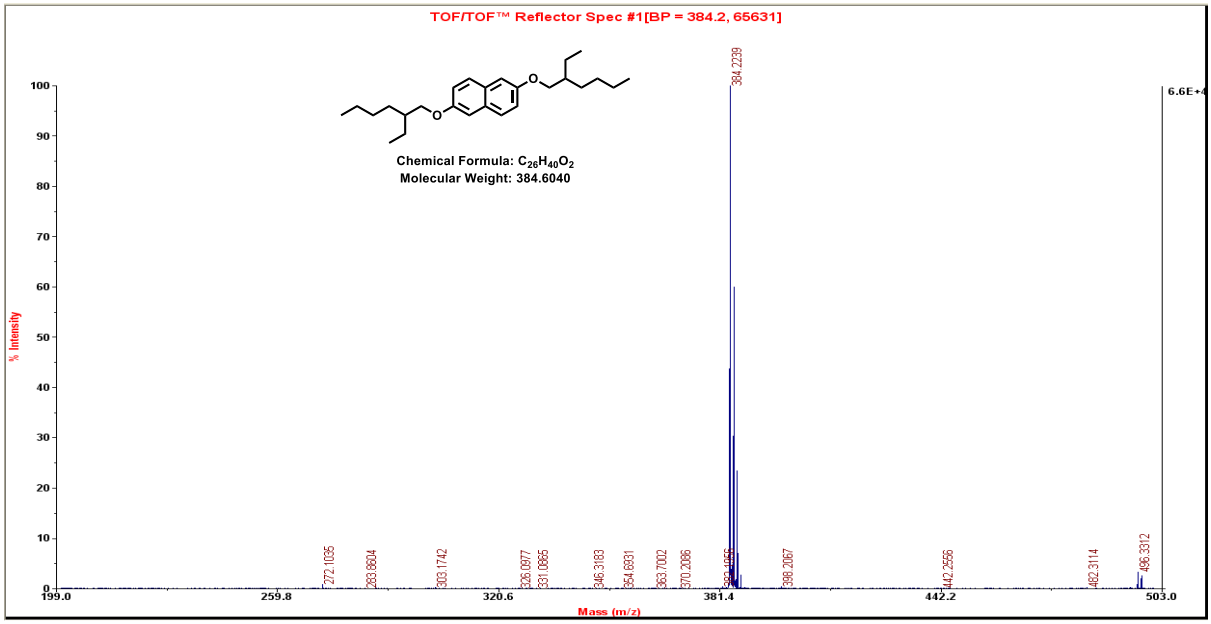
**MALDI-TOF MS**: calcd. for $C_{60}H_{98}N_2O_4$ = 911.4540, found 911.5922.



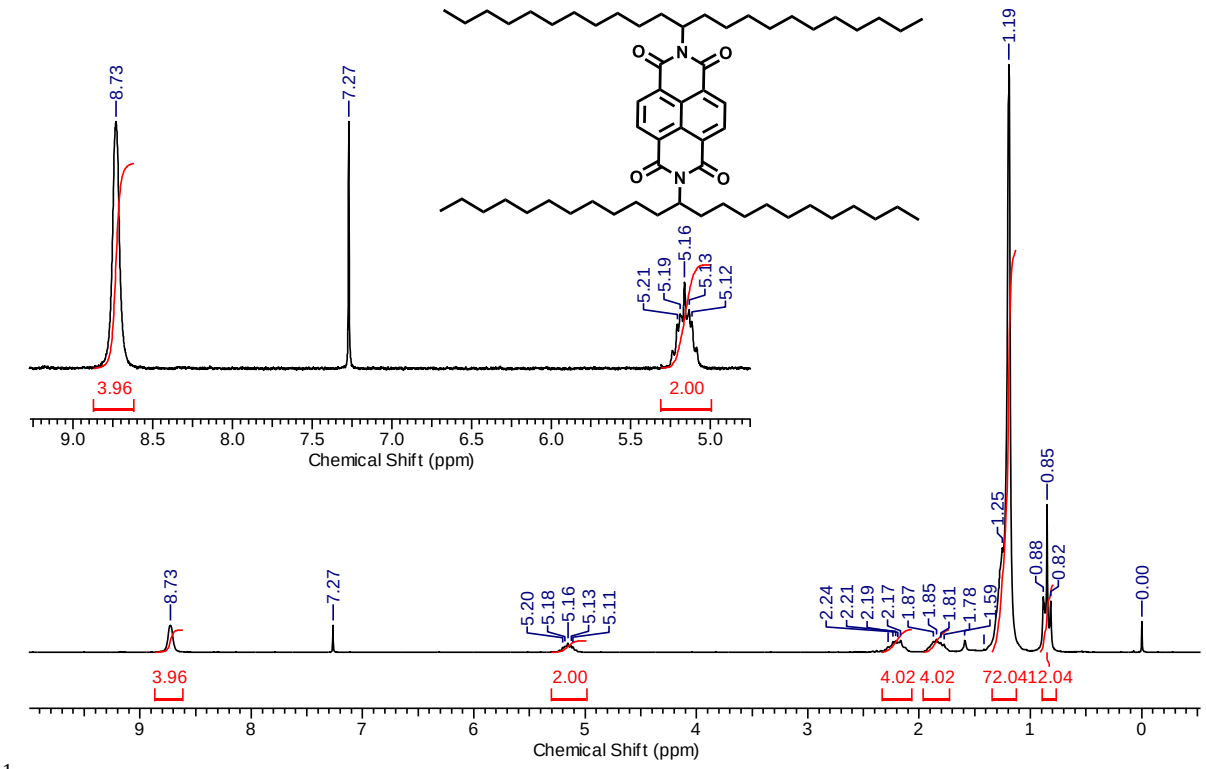

$^1$H NMR spectra of 2,6-bis((2-ethylhexyl)oxy)naphthalene **1**.



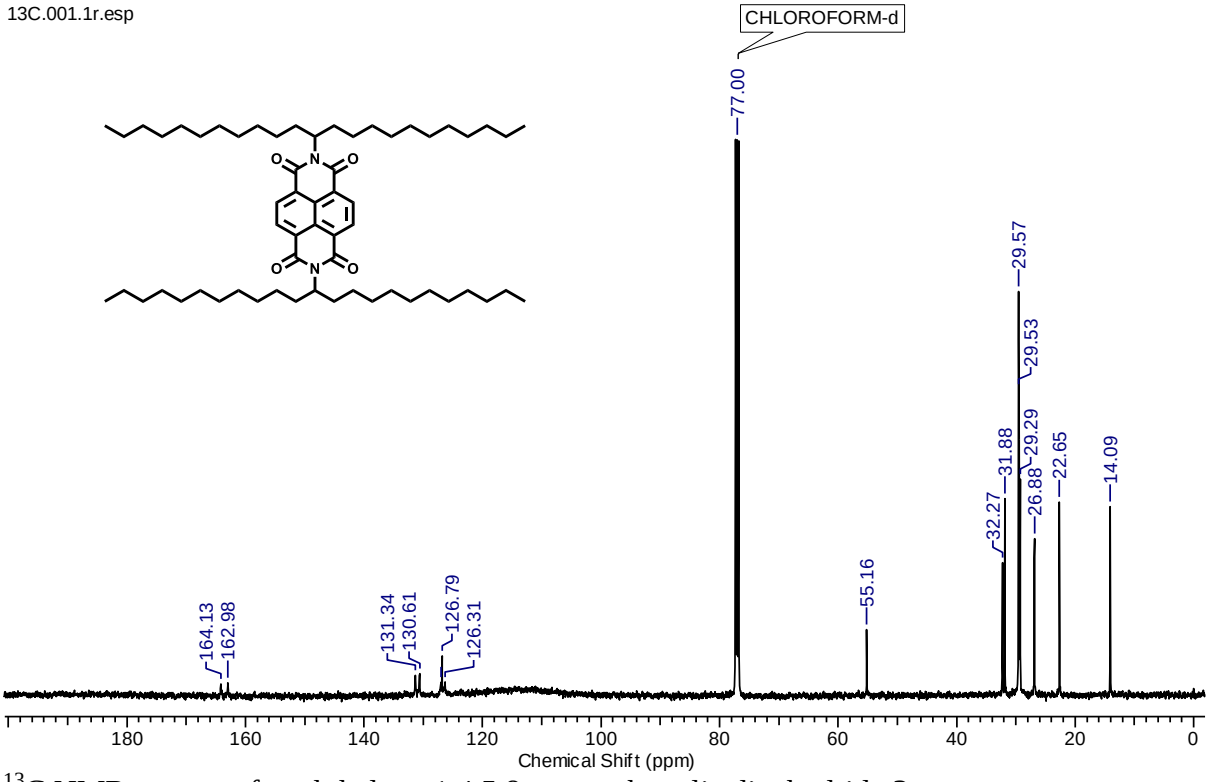

$^{13}$C NMR spectra of 2,6-bis((2-ethylhexyl)oxy)naphthalene **1**.



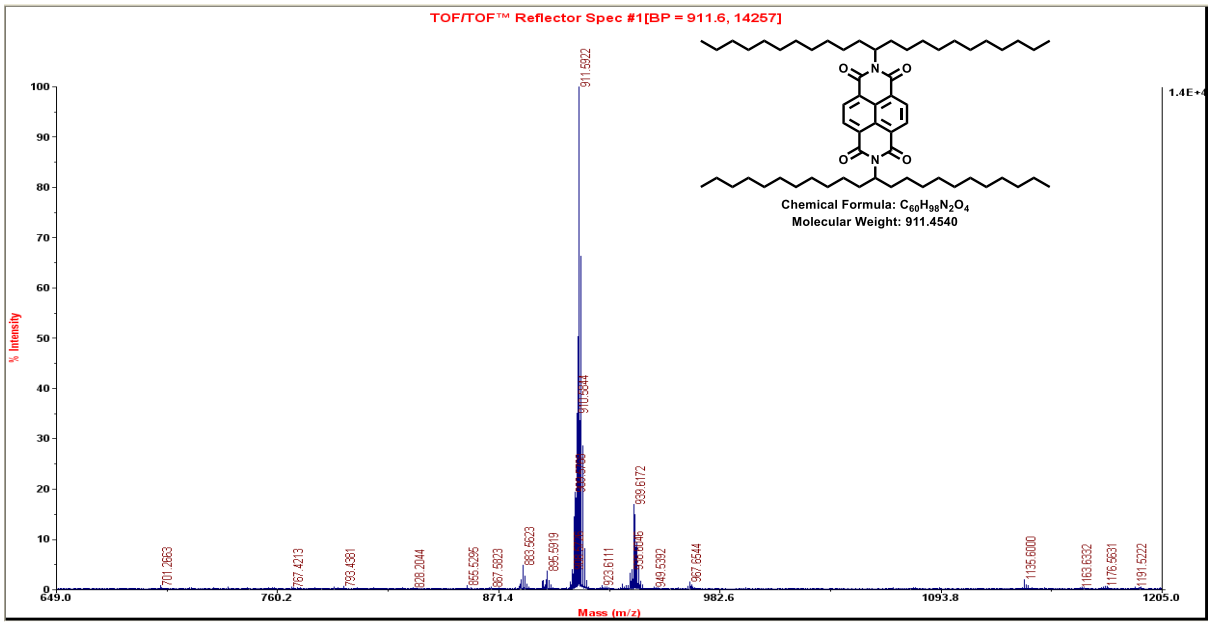

MALDI-TOF MS of 2,6-bis((2-ethylhexyl)oxy)naphthalene **1**.




$^{1}$H NMR spectra of naphthalene-1,4,5,8-tetracarboxylic dianhydride **2**.




$^{13}$C NMR spectra of naphthalene-1,4,5,8-tetracarboxylic dianhydride **2**.



MALDI-TOF MS of naphthalene-1,4,5,8-tetracarboxylic dianhydride **2**.

Synthesis and characterization of molecules **3**[S3], **4**[S4], and **5**[S5] are conducted according to the reported procedures.

# Figures

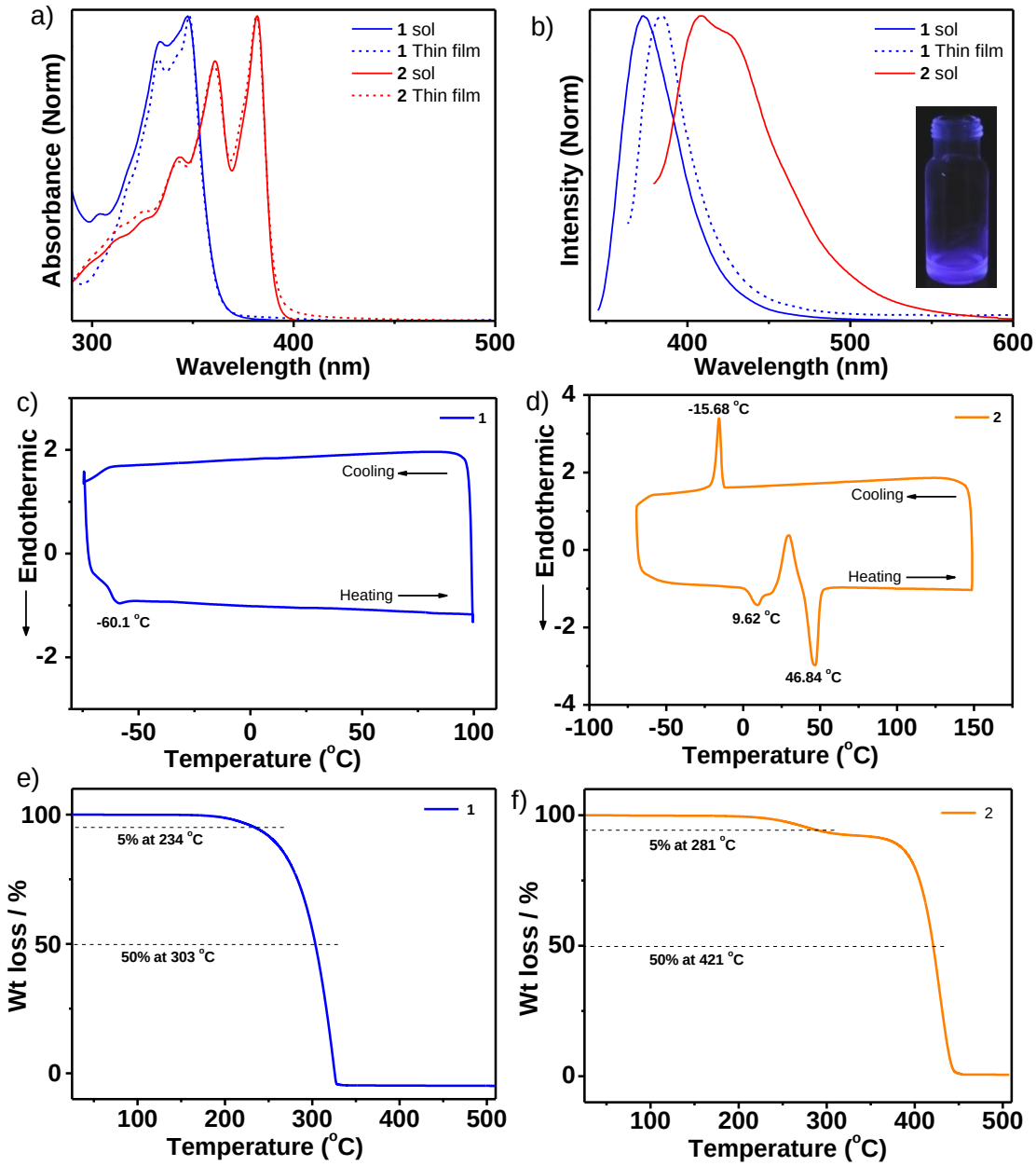



**Figure S1**. a) absorption and b) steady state emission spectra of **1** and **2** in dichloromethane solution and in neat thin film ($\lambda_{ex}$ = 342 nm for **1** and 353 nm for **2**). Inset of Figure S1-b shows the photograph of **1** under UV light (365 nm). c, d) DSC thermograms in the heating trace at a scanning rate of 10 ˚C/min and e, f) TGA of **1** and **2**, respectively.

*Absorption spectra show that both the compounds absorb in the range of 300 to 400 nm (Figure S1-a) and there is no absorption peak between 400 to 600 nm for both the molecules. Both **1** and **2** exhibits almost similar absorption features in solution and thin film. Compound **1** shows an enhanced deep blue emission ranging from 350 to 450 nm with $\lambda_{max}$ located at 372 nm (Figure S1-b). NDI derivative **2** exhibited a comparatively broad emission from 370 to 550 nm, which is nearly 30 nm red shifted to that of 1. However, in the neat form only compound **1** is found to be emissive (Inset; Figure S1-b).*

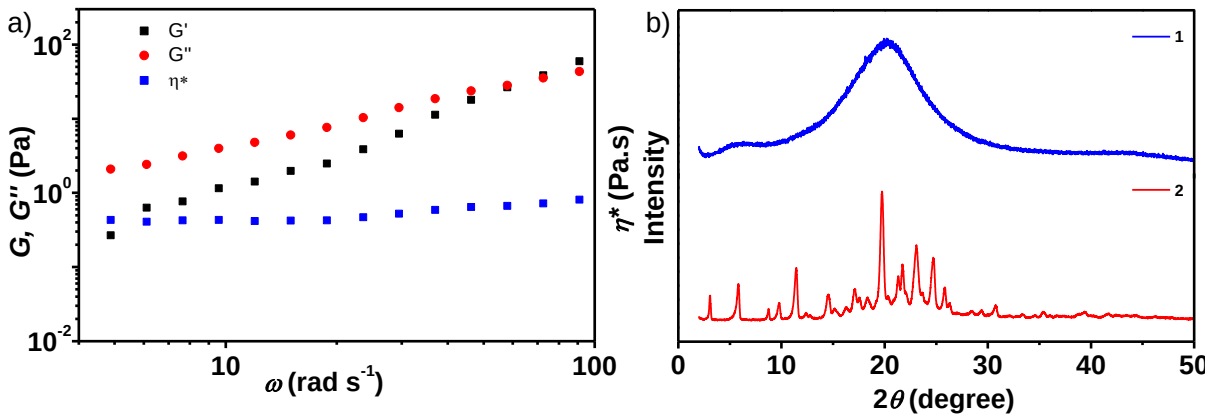



**Figure S2**. a) Variation of storage modulus ($G'$) (■), loss modulus ($G''$) (●) and complex viscosity ($\eta^*$) (■) versus angular frequency on double logarithmic scale, of **1**. b) Comparison of PXRD pattern of **1** and **2**.

*We prepared a series of acceptor molecules (even donor and acceptor with same branched alkyl chain) and except molecules **2**, none found as RT liquid. Molecule **2** with long branched chain is a low melting solid giving diffraction peaks in PXRD at RT, not a free flowing liquid. However, we found that **2** is a free flowing liquid above 46 °C.*

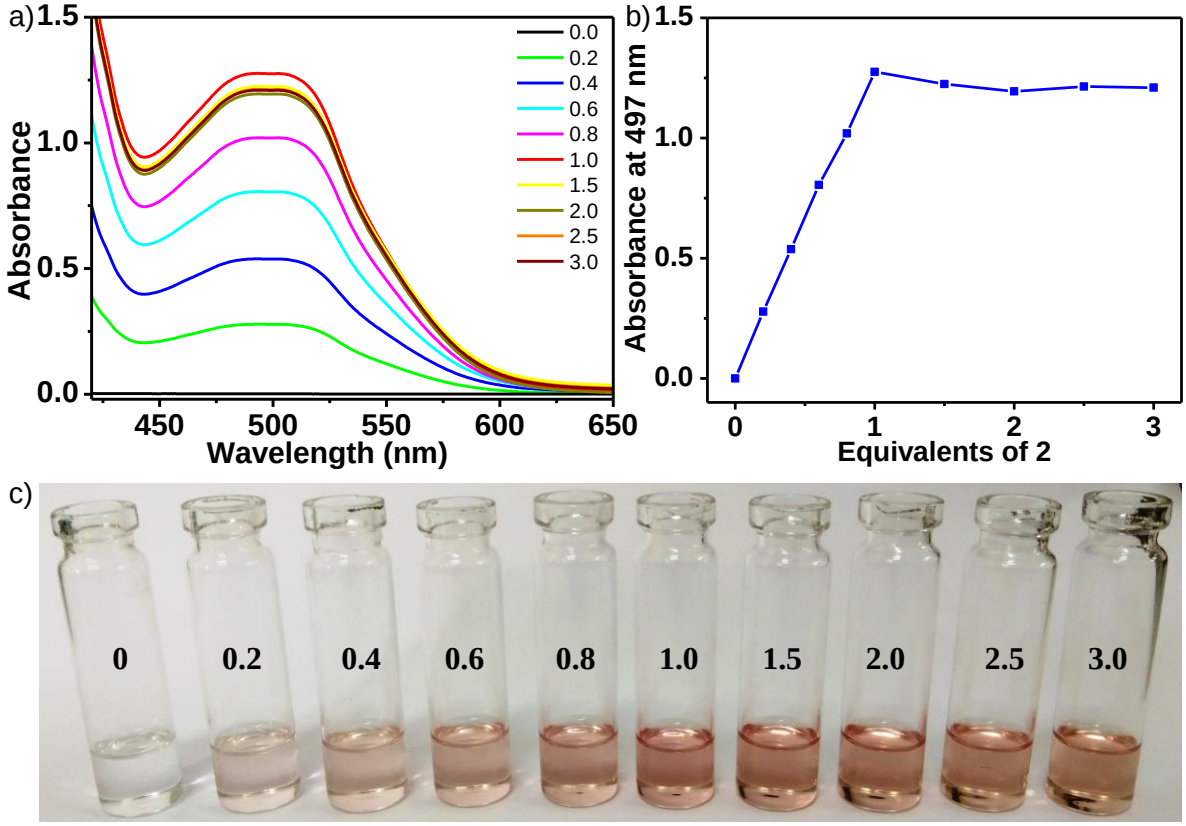



**Figure S3.** a) Variation in absorption spectra of **1** in *n*-hexane (25 mM) with increasing equivalents of **2** in *n*-hexane at 25 ˚C, b) corresponding variation of absorbance at 497 nm with increasing equivalents of **2**. c) Photographs of the CT complex with varying equivalents (0 to 3) of acceptor **2**.

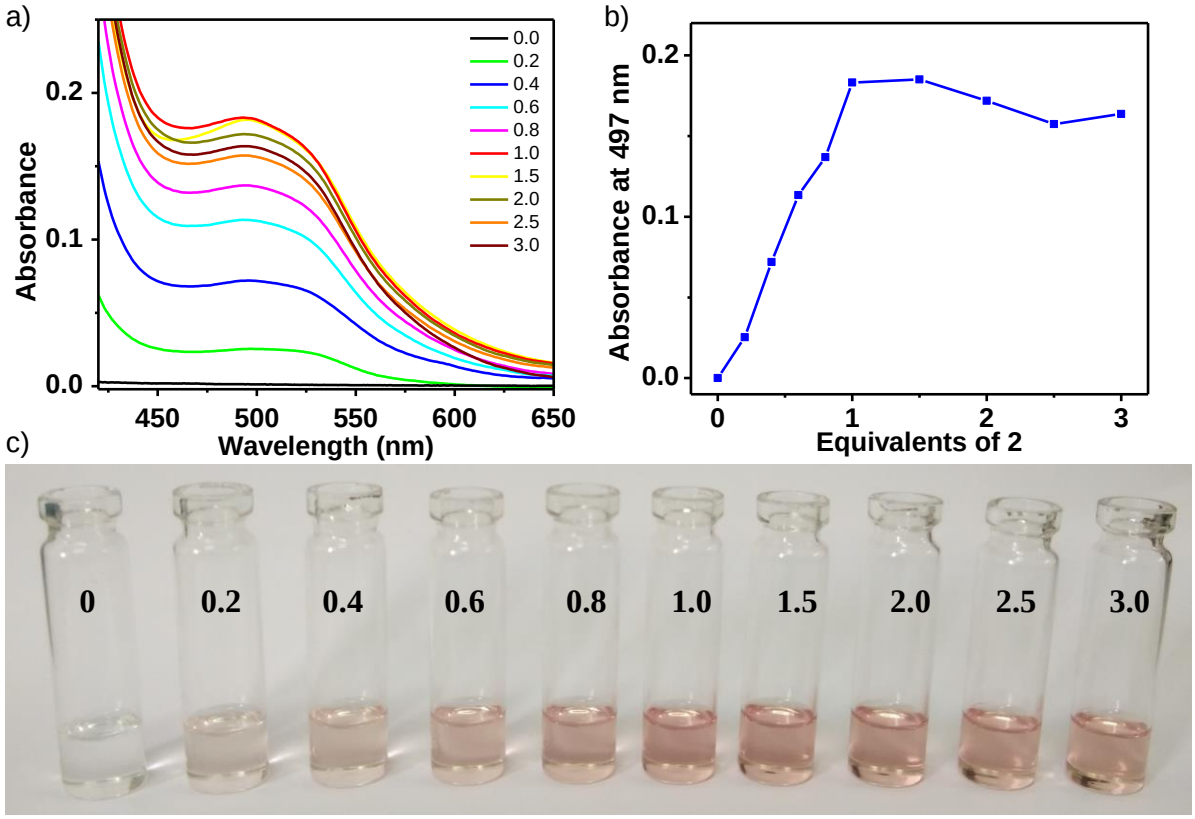



**Figure S4.** a) Variation in absorption spectra of **1** in dichloromethane (25 mM) with increasing equivalents of **2** in dichloromethane at 25 ˚C, b) corresponding variation of absorbance at 497 nm with increasing equivalents of **2**. c) Photographs of the CT complex with varying equivalents (0 to 3) of acceptor **2**.

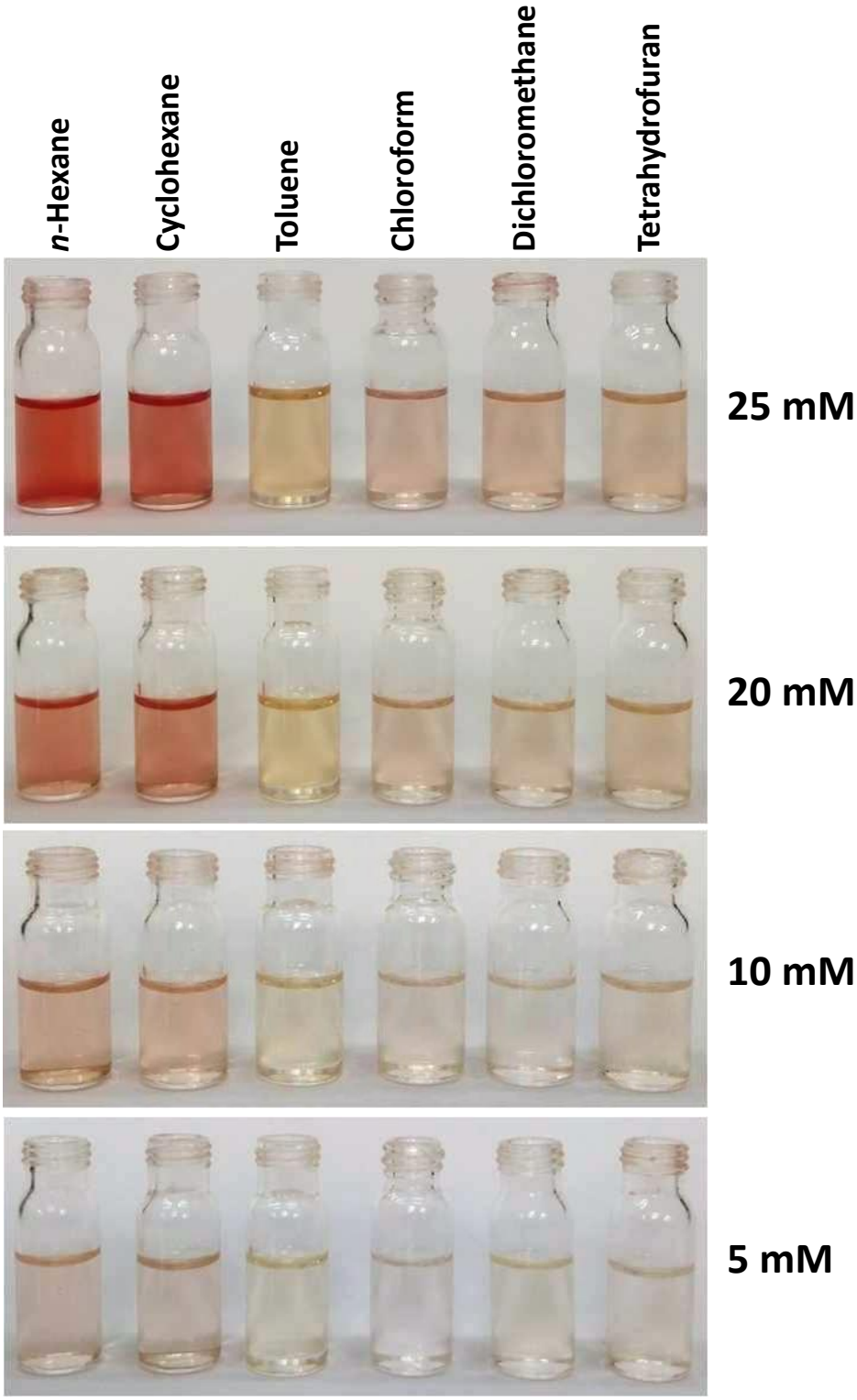



**Figure S5.** Photographs of the **1**+**2** (1:1) CT complex in various solvents at different concentrations.

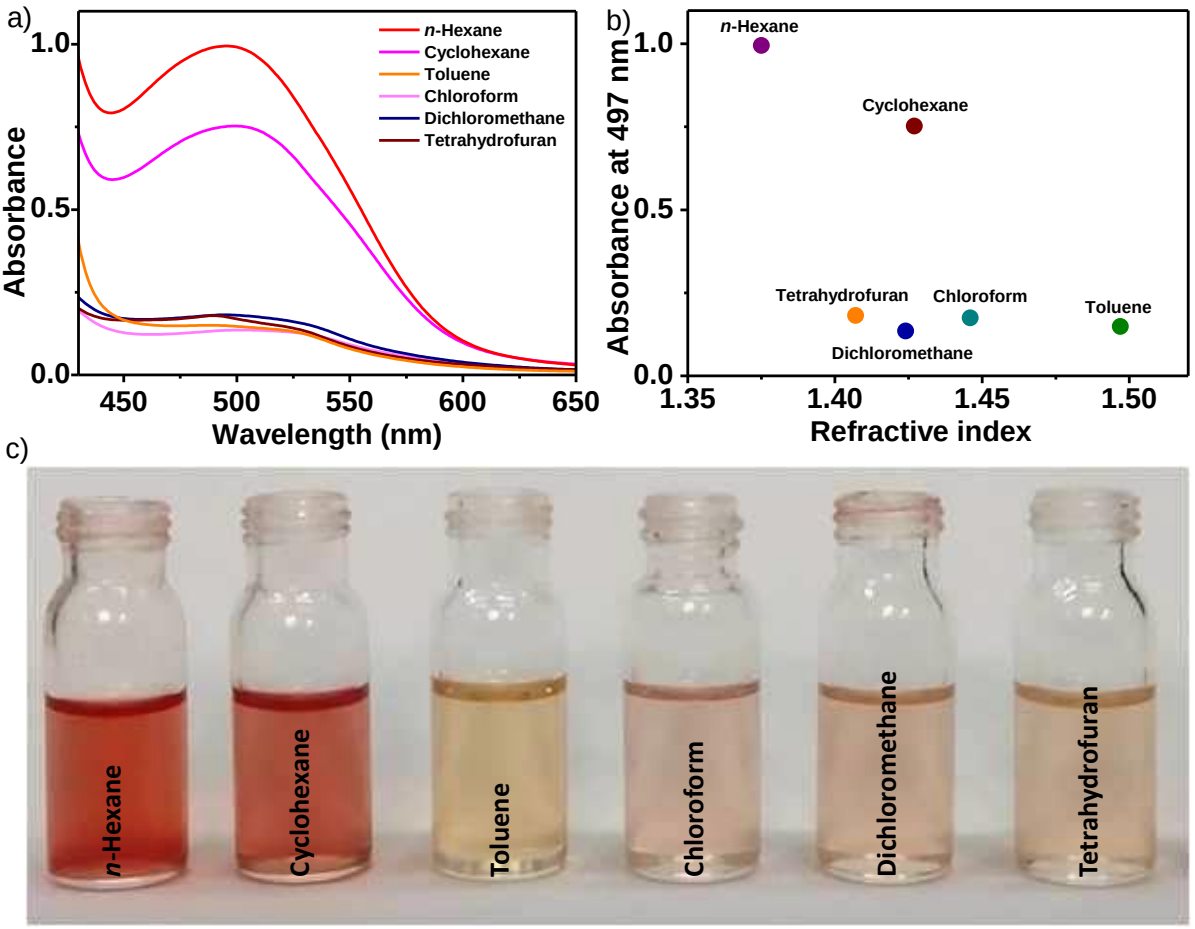



**Figure S6.** a) UV-Vis absorption spectra of **1**+**2** (1:1) CT complex in various solvents (25 mM) and the corresponding variation of absorbance at $\lambda$ = 497 nm against refractive index of the solvents. Photographs of the **1**+**2** (1:1) CT complex in various solvents (25 mM) showing the variation of CT complex colour.

*A clear decrease in the CT band intensity shows that the complexation is primarily due to electrostatic interaction between the donor-acceptor. It has to be noted that polar solvents can efficiently disrupt the electrostatic attraction unlike nonpolar solvents. Hence, n-hexane and cyclohexane stabilize the CT complex compared to other polar solvents.*

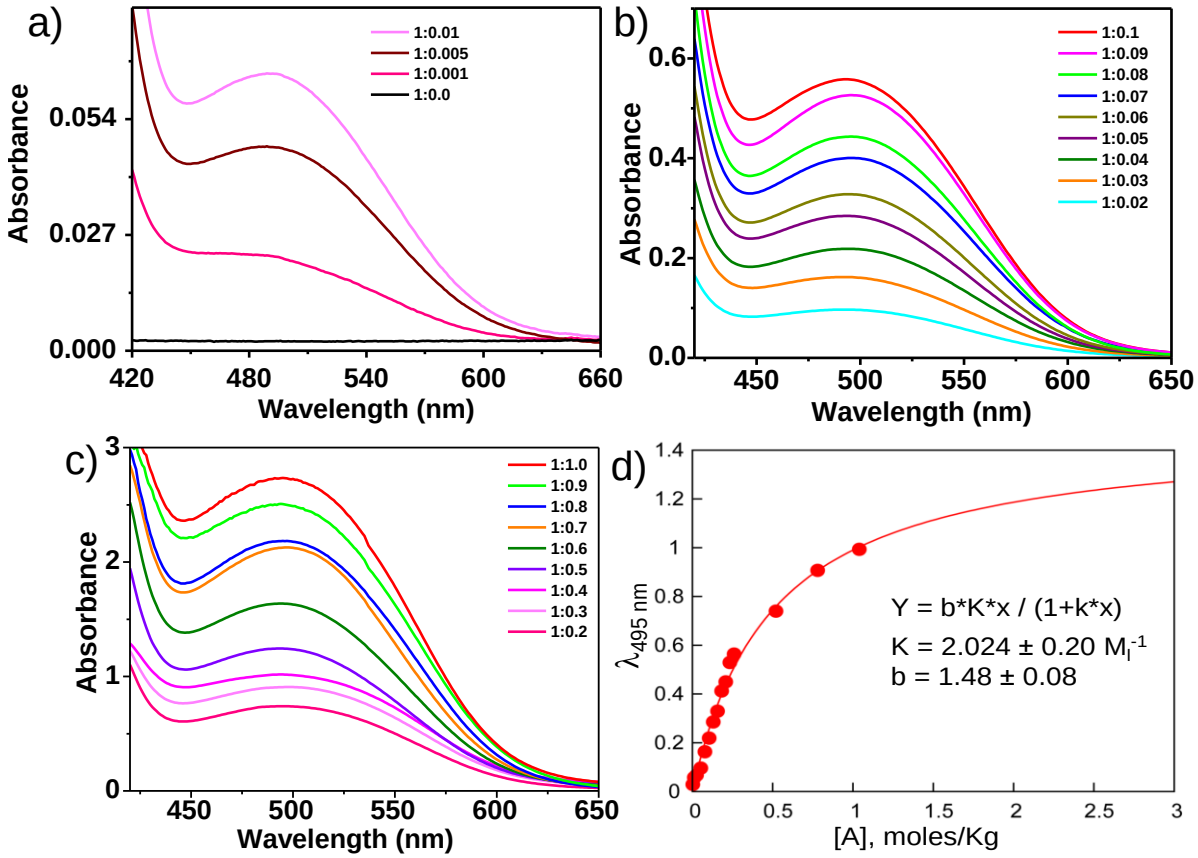



**Figure S7.** Absorption spectral variation of **1**+**2** CT liquid with increasing equivalents of **2** ranging from a) 1:0.0 to 1:0.01, b) 1:0.02 to 1:0.1 and c) 1:0.2 to 1:1.0 in the solvent-free condition. d) Relative variation of $\lambda_{max}$ at 495 nm with respect to neat donor as a function of acceptor concentration at RT.

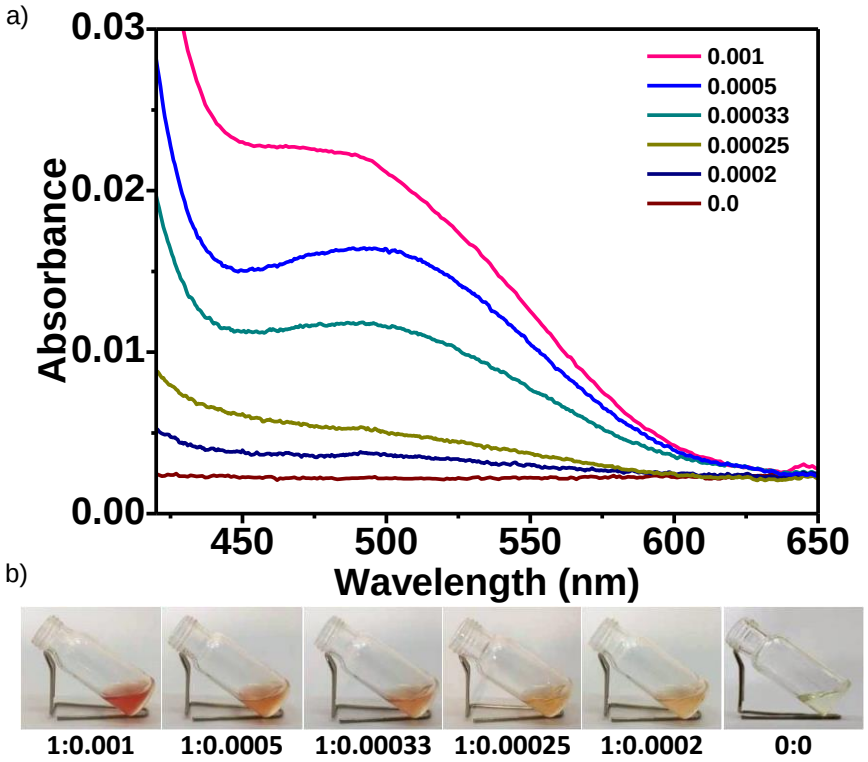



**Figure S8.** a) Absorption spectral variation of **1**+**2** CT liquids with increasing equivalents of **2** ranging from 0.0002 to 0.001 equivalents and b) corresponding photographs of CT liquids of **1** and **2**.

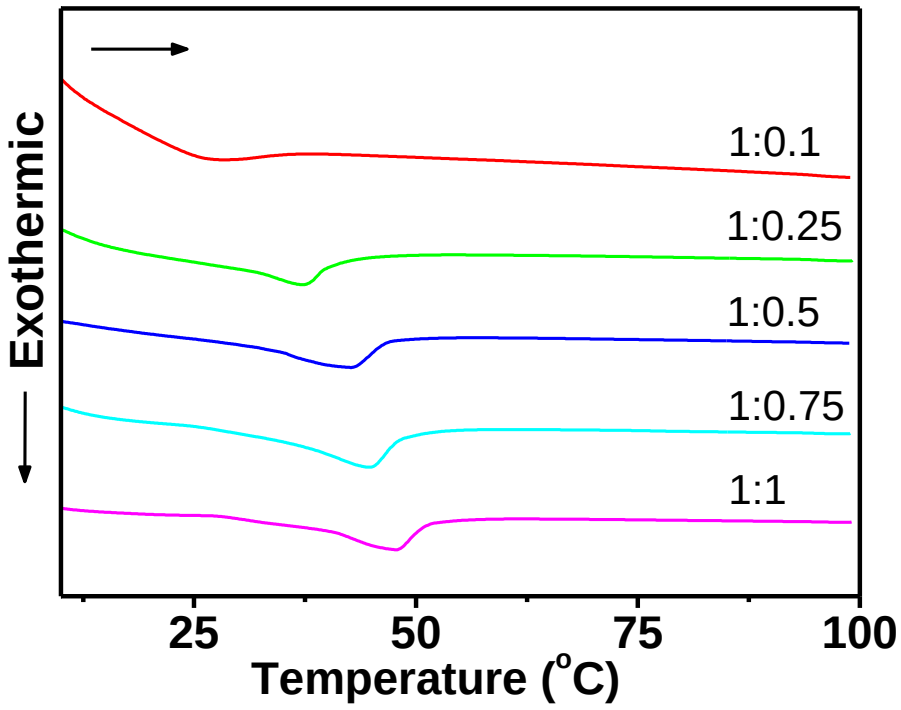



**Figure S9.** DSC thermograms in the heating trace of **1**+**2** CT liquids with varying equivalents of **2** at a scanning rate of 10 ˚C/min.

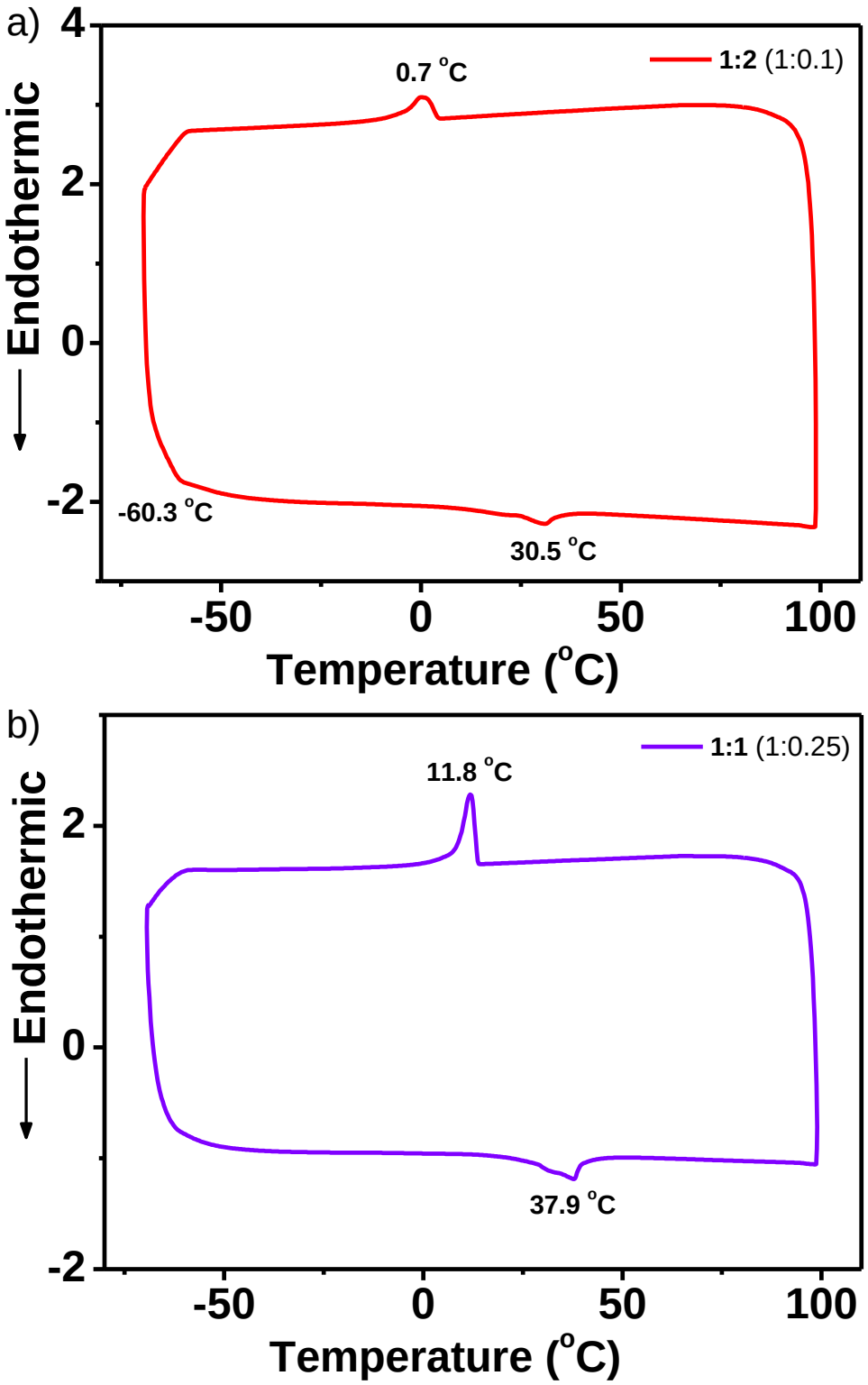



**Figure S10**. DSC thermograms of **1**+**2** CT liquid with varying acceptor ratio, a) 1:0.1 and b) 1:0.25 at a scanning rate of 10 ˚C/min.

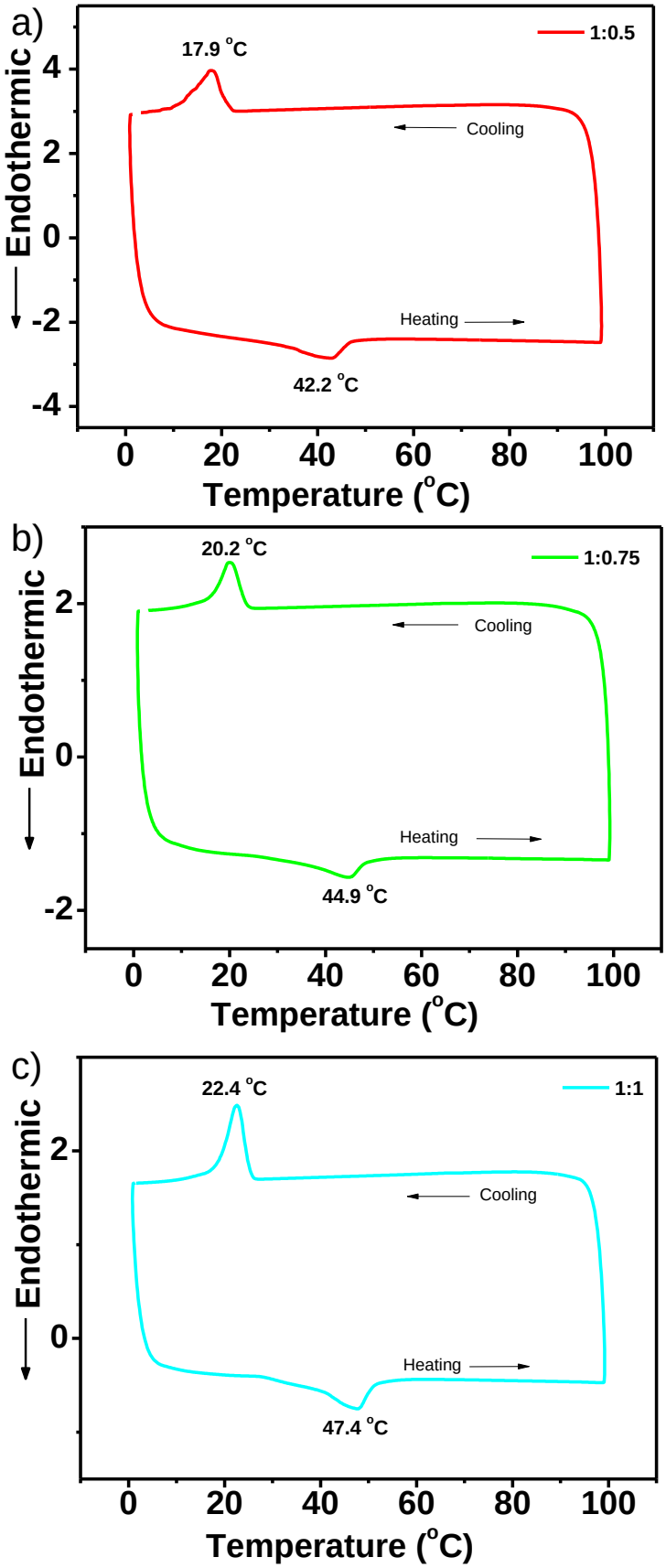



**Figure S11**. DSC thermograms of **1**+**2** CT liquid with varying acceptor ratio, a) 1:0.5, b) 1:0.75 and c) 1:1 at a scanning rate of 10 ˚C/min.

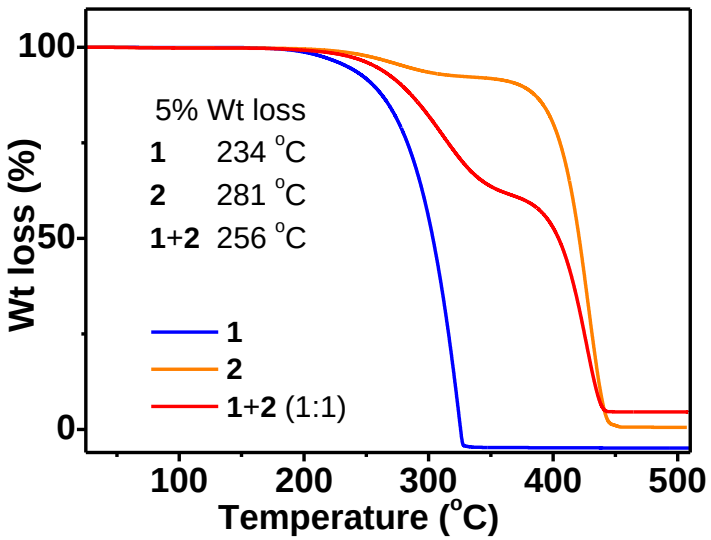



**Figure S12.** TGA analysis of **1**, **2** and **1**+**2** (1:1) CT liquid.

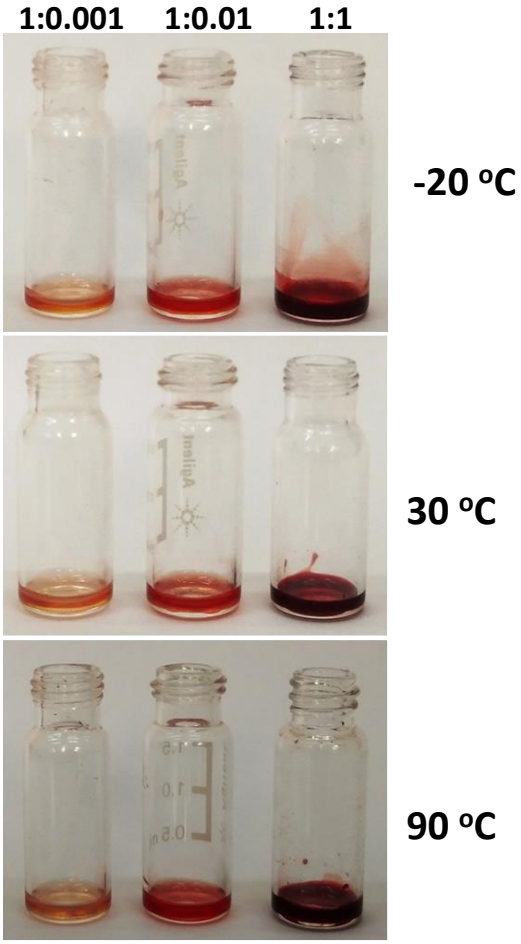



**Figure S13**. Photographs of the **1+2** CT liquids with varying D-A ratio stored at three different temperatures, a) -20 ˚C (freezer), b) 30 ˚C (RT) and c) 90 ˚C (oven) for two months.

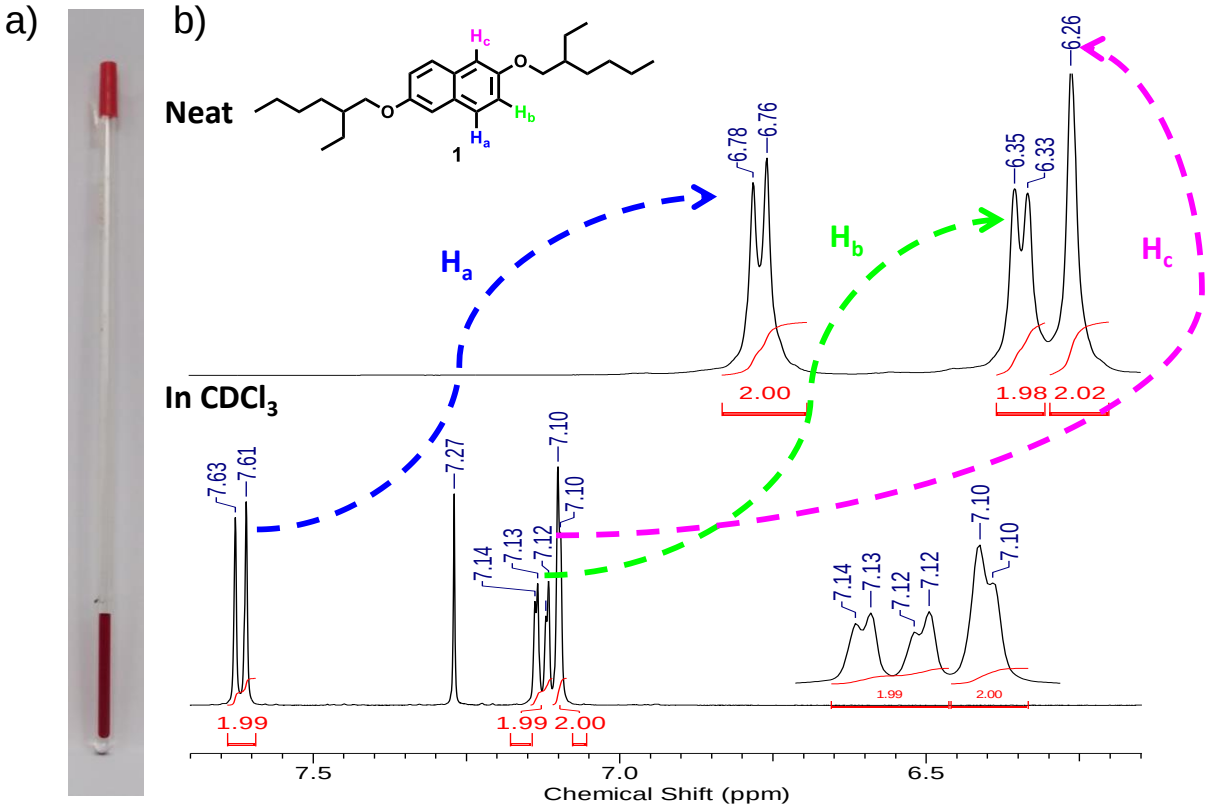



**Figure S14**. a) Photograph of the 3 mm NMR tube containing **1+2** CT liquid inside the 5 mm NMR tube with DMSO-$d_6$ as an external lock used for all NMR studies. b) Comparison of $^1$H NMR spectra of **1** as neat and in $CDCl_3$ solution.

*Comparison of the $^1$H NMR spectra of the donor molecule in $CDCl_3$ and in the neat state (external reference DMSO-d6), show that all signals shift upfield. The proton Ha at 7.63 (2H, d, J = 8.7 Hz) shift to 6.78 (2H, d, J = 8.9 Hz) and becomes broad compared to spectrum in $CDCl_3$. The Hb proton showing doublet of doublets at δppm 7.14 with large ortho coupling 8.7 Hz and small meta coupling 2.26 Hz, shifts to 6.35 showing a doublet with coupling constant 8.9 Hz. Proton Hc which shows a doublet (J = 2.26 Hz) at δppm 7.10 appears as a broad singlet at δppm 6.26.*

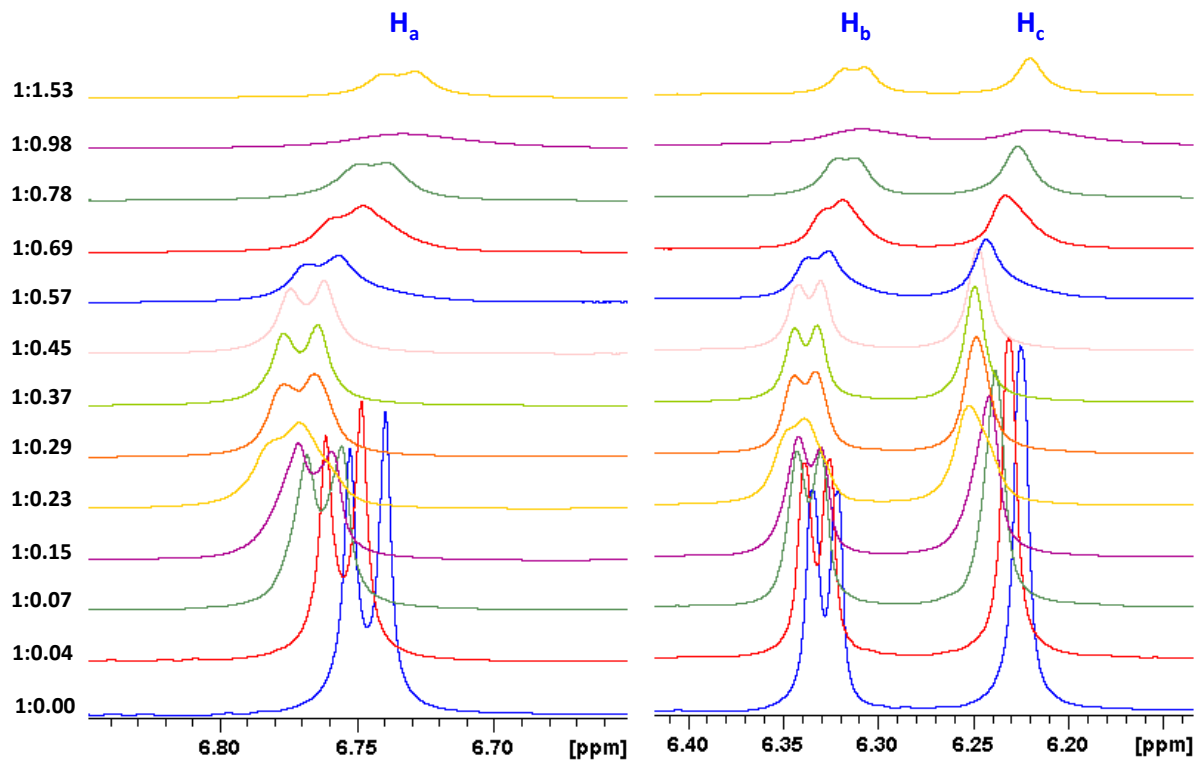



**Figure S15**. Expansion of $^{1}$H NMR titration spectra recorded at 318 K, showing donor **1** proton signals in the aromatic region.

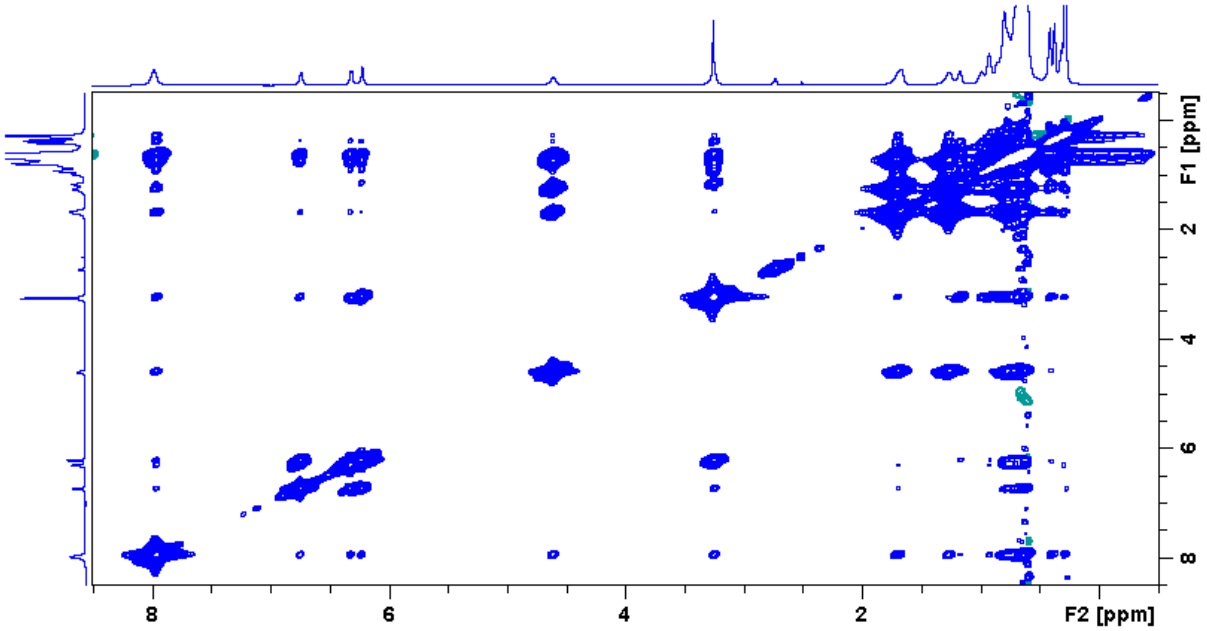



**Figure S16.** NOESY spectrum of the **1**+**2** (1:0.98) CT liquid at 318 K. Mixing time is 30 ms, for which spin diffusion effects are minimal.

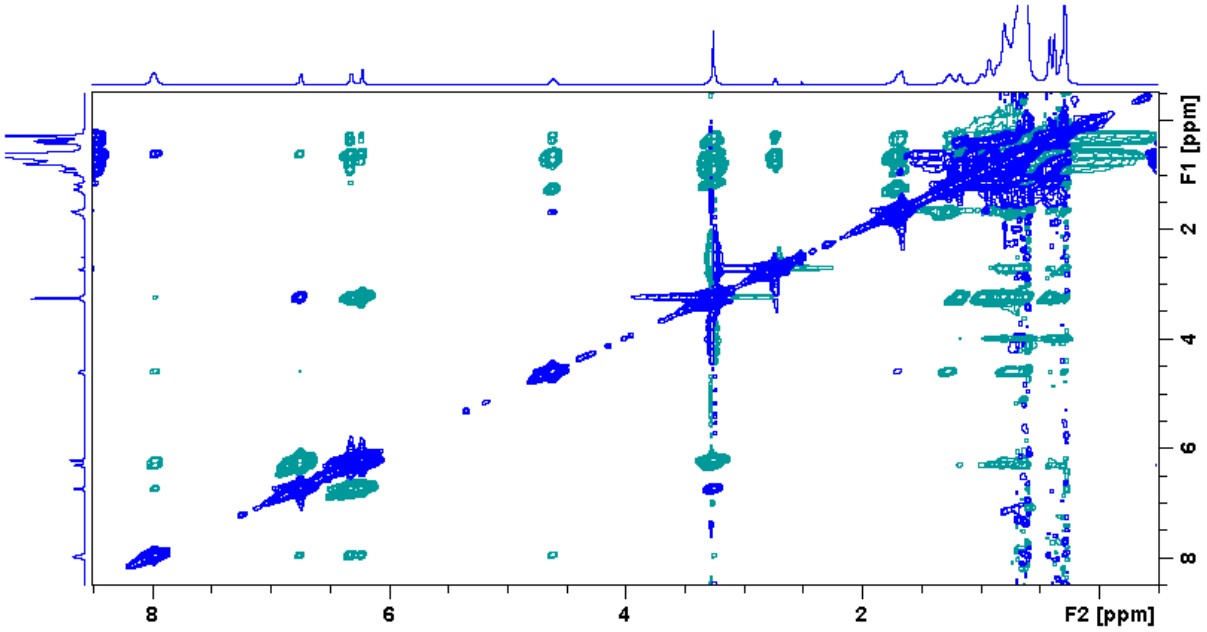



**Figure S17**. ROESY spectrum of the **1**+**2** (1:0.98) CT liquid at 318 K. Spin-lock strength and duration is 2.5 KHz and 100 ms, respectively.

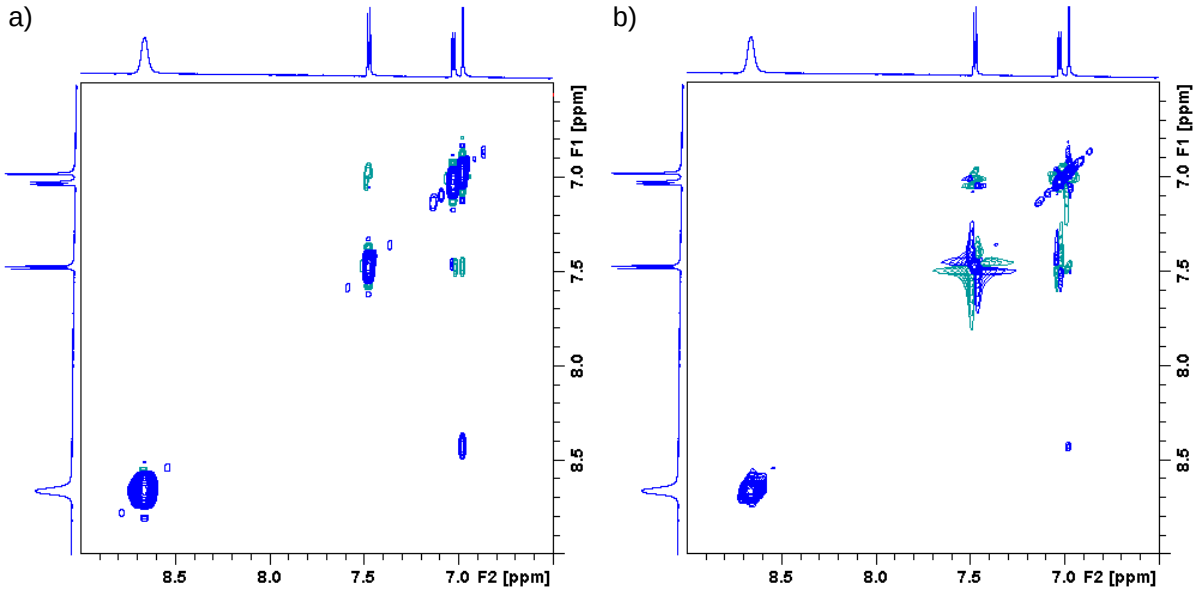



**Figure S18**. 2D NMR spectra a) NOESY and b) ROESY of **1**+**2** (1:1) CT complex in *n*-hexane (25 mM) at 318 K.

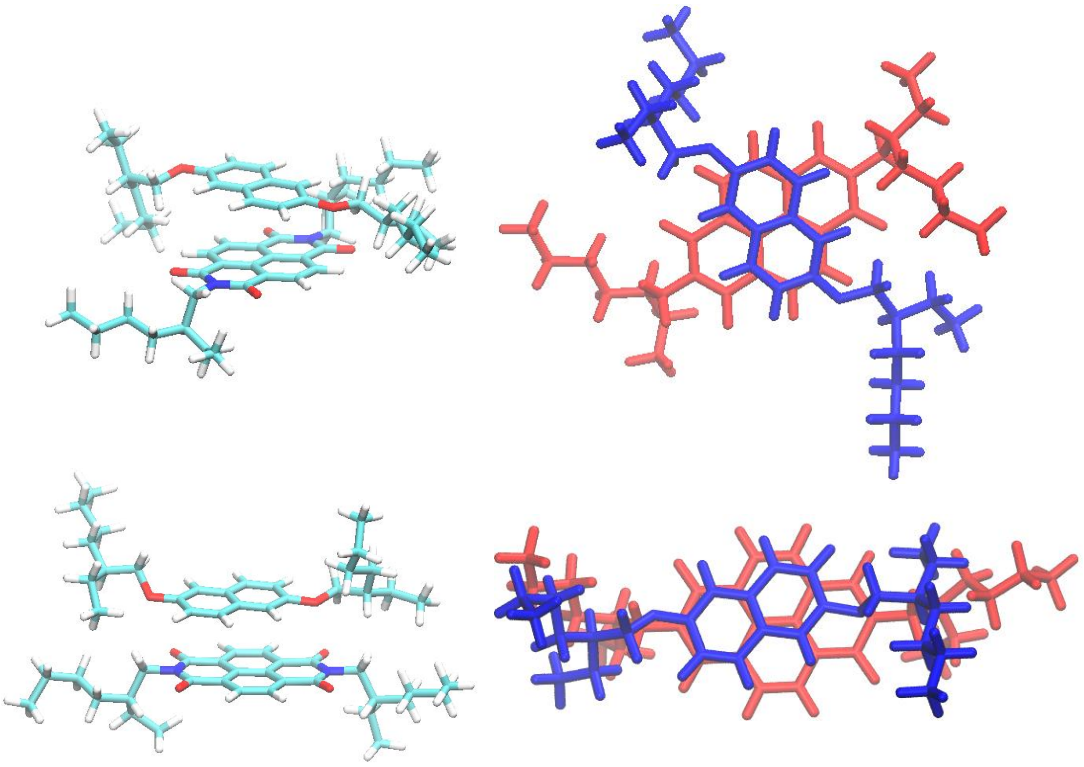


**Figure S19**. Two Preferred orientations in the D-A complex obtained from MD simulation.

*A near perpendicular stacking is more populated/stable in the MD simulation possibly due to less steric repulsion between the long alkyl chains. In parallel stack, due to repulsion between the chains stacking may be a bit distorted. Also, the two aromatic rings of donor need to align above the four rings of acceptor, hence a staggered alignment of the central axis of the molecules is likely.*

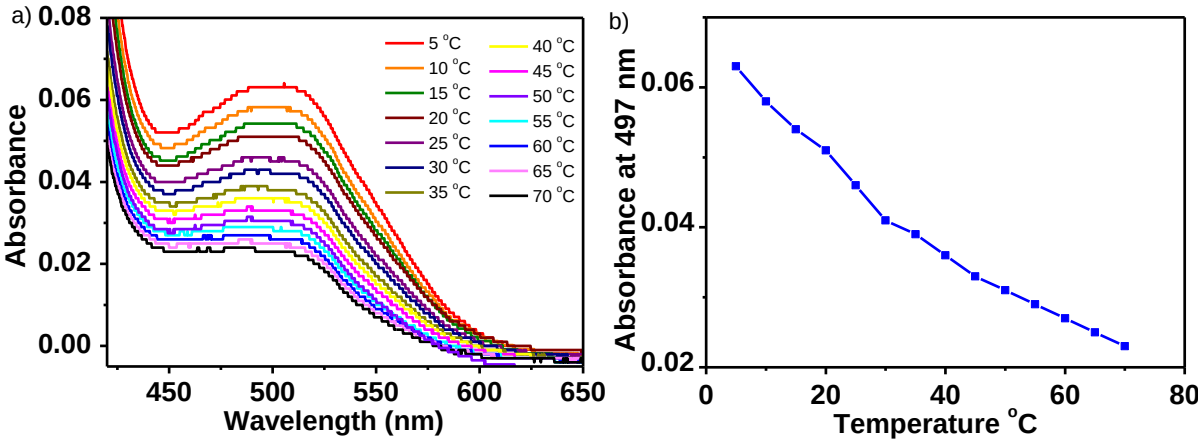



**Figure S20**. a) Temperature dependent absorption spectral changes of the **1**+**2** (1:1) CT complex in cyclohexane (3 mM) and b) the corresponding variation of absorbance at 497 nm with temperature.

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