Supporting Information

Chain Folding of Carbazole-Donor Containing Polymers via Two-point Interaction with Naphthalene monoimide-based Acceptors

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Experimental Section

Material and methods

Carbazole, 1,8-naphthalic anhydride, (±)-β-citronellol, S-(-)-β-citronellol, 1-bromooctane, 2-ethylhexyl bromide, and tetraethyleneglycol were purchased from Sigma-Aldrich. Propargyl alcohol, TBAB, n-propylamine, pyridine, and NaN_3 were purchased from Spectrochem. All the remaining salts and reagents were purchased from other commercial sources (Spectrochem, SDFCL) and used directly unless mentioned otherwise. All organic solvents were procured from SDFCL or AVRA Synthesis Pvt Ltd, dried, and distilled when required. All intermediates, monomers, and polymers were characterized by ^{1}H NMR spectroscopy using a Bruker AV 400 MHz or 500MHz spectrometer in suitable deuterated solvents; TMS was used as an internal reference. A Shimadzu 2600 UV-visible spectrophotometer was used to record all the UV measurements.

Spectroscopic titration studies

^{1}H-NMR titration experiments were performed in 1:2 ratio of $CDCl_3$: CH_3CN (v/v) solvents whereas in the UV-Visible titration experiments 1:2 ratio of $CHCl_3$: CH_3CN (v/v) solvents were used.

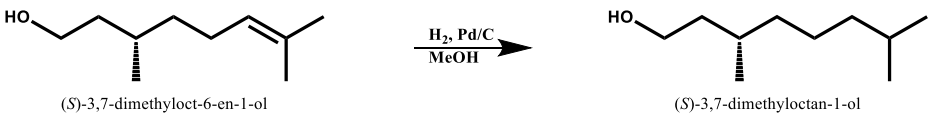
The NMR titration experiments were carried out at a constant concentration of the polymer; therefore, all the donor solutions were prepared using a stock solution of the polymer solution. At first, a stock solution of polymer (1.2ml) was prepared, and 0.5ml of this stock solution was then transferred to an NMR tube. An acceptor (folding agent) solution that is 10-15 times higher in concentration was prepared from the initial polymer solution. Acceptor solutions were then added successively to the NMR tube containing the polymer. Each new sample was analyzed by ^{1}H-NMR spectroscopy. All volumes were quantified by weighing; the weight differences were estimated and used for the calculation of the concentrations. Hamilton syringes were used to transfer the required volume during titration experiments.

For the UV-visible titration experiments, an equimolar solution (1.5 ~ 2 mM) containing Donor-polymers (considering repeating unit molecular weight) and different folding agents was prepared in 1:2 $CHCl_3$:CH_3CN (v/v) solvent and 1 ml of this equimolar solution was transferred to a 1.5 ml cuvette. The resulting solution was then subjected to a serial dilution; in each step, 100 µL was pipetted out from the cuvette, and 100 µL of 1:2 $CHCl_3$:CH_3CN (v/v) solvent mixture was added to it, and UV-visible spectra were recorded in each dilution step.

Synthesis of intermediate molecules for carbazole-based AB_2 monomer

3,6-Dibromo-9H-carbazole, 3,6-dimethoxy-9H-carbazole, 3,6-dimethoxy-9-alkyl-carbazole were synthesized following the procedure mentioned in the literature.[1]

(S)-3,7-Dimethyloctan-1-ol



(*S*)-3,7-dimethyloct-6-en-1-ol (*S*)-3,7-dimethyloctan-1-ol

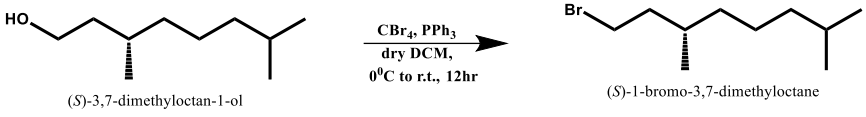
(S)-3,7-Dimethyloct-6-en-1-ol (1gm, 6.4mmol) was taken in 80 ml dry MeOH, and 50mg of Pd on activated charcoal was added to the solution. An H_2 balloon was connected to the round bottom flask (RB) and the solution was stirred at room temperature for 12 hours. Once the hydrogenation was over, the solution mixture was passed through a celite bed to remove the catalyst and charcoal. After removing the solvent under reduced pressure, a white solid product was recovered.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 3.72-3.63 (m, 2H, -**CH2**OH); 1.54-1.50 (m, 8H, -**CH2** of C2, C4, C5, C6 atoms); 1.16-1.10 (m, 2H, -**CH**); 0.89-0.85(m, 9H, -**CH3**).

Using the same synthetic protocol racemic 3,7-dimethyloctan-1-ol was synthesized.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 3.7-3.61 (m, 2H, -**CH2**OH); 1.63-1.20 (m, 8H, -**CH2** of C2, C4, C5, C6 atoms); 1.15-1.09 (m, 2H, -**CH**); 0.89-0.84(m, 9H, -**CH3**).

(S)-1-Bromo-3,7-dimethyloctane



(*S*)-3,7-dimethyloctan-1-ol (*S*)-1-bromo-3,7-dimethyloctane

In a 100 ml RB 1.14gm (7.2mmol) of (s)-3,7-dimethyloctanol and 2.63gm (7.92mmol) of CBr_4 were taken in 50ml DCM. Under ice-cold conditions, 2.27gm (8.64 mmol) of PPh_3 was added and stirred in the solution mixture for 30 min at ice-cold conditions and another 12 hours at room temperature. The reaction was quenched with H_2O and then the product was extracted in $CHCl_3$. The organic layer was passed through Na_2SO_4 and after evaporation of solvent under reduced pressure a viscous brownish liquid was obtained. The obtained product was further purified by kugelrohr distillation which resulted in a clear viscous liquid product.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 3.49-3.37 (m, 2H, -**CH2**Br); 1.92-1.82 (m, 1H, -**CH**CH3CH3); 1.71-1.59 (m, 2H, -**CH2**CH2Br); 1.57-1.47 (m, 1H, -**CH**CH3); 1.33-1.09(m, 6H, -**CH2**); 0.89-0.86 (m, 9H, -**CH3**).

Using a similar procedure racemic 1-bromo-3,7-dimethyloctane was synthesized.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 3.49-3.36 (m, 2H, -**CH2**Br); 1.91-1.84 (m, 1H, -**CH**CH3CH3); 1.70-1.59 (m, 2H, -**CH2**CH2Br); 1.56-1.48 (m, 1H, -**CH**CH3); 1.35-1.08(m, 6H, -CH**CH2CH2CH2**CH); 0.89-0.86 (m, 9H, -**CH3**).

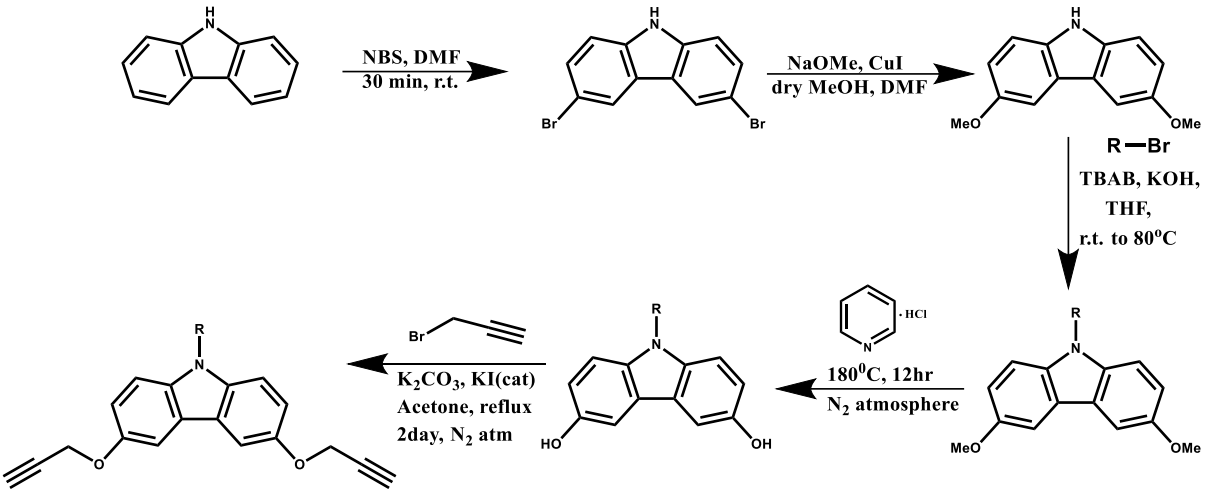
3,6-Dihydroxy-9-octyl carbazole

3,6-Dihydroxy-9-octyl carbazole was synthesized by reacting pyridinium hydrochloride salt with 3,6-dimethoxy-9-octyl carbazole in its melted state. The pyridinium hydrochloride salt was prepared by passing HCl gas through an ether (dry) solution containing pyridine. Precipitated highly hygroscopic salt was recovered by evaporating the ether under reduced pressure. Obtained white salt was directly used in the reaction. In a typical procedure, 3,6-dimethoxy-9-octyl carbazole (2.71gm, 7.98mmol) was taken in a 100ml RB and 15 equivalent of pyridinium salt (13.84gm, 119.74mmol) was added to it. The solid mixture was heated at 180°C for 12hr under N_2 atmosphere. The reaction was cooled down to room temperature and quenched with H_2O. The product was extracted in EtOAc and the collected organic layer was passed through Na_2SO_4. The solvent was removed under reduced pressure and after drying an off-white solid product was recovered. The obtained product was further purified by column chromatography using a hexane/EtOAc solvent combination.

^{1}H-NMR (400 MHz, DMSO-d6, δ ppm): 8.85 (s, 2H, -O**H**); 7.3-7.26 (q, 4H, -Ar**H**); 6.89-6.87 (q, 4H, -Ar**H**); 4.21-4.19 (t, 2H, -N**CH2**); 1.69-1.64 (t, 2H, -NCH2**CH2**); 1.24-1.17 (m, 10H, -**CH2** of C8 alkane functional group); 0.83-0.8 (t, 3H, -**CH3**).

Similarly, 3,6-dihydroxy-9-((±)-citronelly) carbazole, 3,6-dihydroxy-9-(s-(-)-citronelly) carbazole, 3,6-dihydroxy-9-(2-ethylhexane) carbazole were synthesized.

Synthesis of dipropargyl monomer



Scheme S1: *Synthesis scheme for the dipropargyl containing carbazole-based AB_2 monomer.*

3,6-Dipropargyl-9-octyl carbazole

For the synthesis of dipropargyl monomer, 0.725gm (2.33mmol) of 3,6-dihydroxy-9-octyl carbazole, 1.29gm (9.32mmol) of K_2CO_3, and 0.69gm (5.82mmol) of propargyl bromide were taken in 30ml of acetone and catalytic amount (20mg) of KI was added. The mixture was refluxed for 2 days under N_2 atmosphere. Acetone was evaporated under reduced pressure and then $CHCl_3$ was added to it. The $CHCl_3$ soluble part was separated and concentrated by removing the solvent under reduced pressure. A white crystal was recovered from the concentrated solution when kept at room temperature overnight. Crystals were separated and rinsed twice with fresh $CHCl_3$ and after drying thoroughly a white solid product was obtained. The product was further purified by column chromatography using an EtOAc/hexane solvent combination.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.63(d, 2H, -Ar**H**); 7.3-7.26(d, 2H, -Ar**H**); 7.18-7.15(d, 2H, -Ar**H**); 4.8(d, 4H, -**CH2**CCH); 4.23(t, 2H, -N**CH2**); 2.54 (t, 2H, -C**CH**); 1.84-1.80 (t, 2H, -NCH2**CH2**); 1.36-1.23 (m, 10H, -**CH2** of C8 alkane functional group); 0.86(t, 3H, -**CH3**).

Other monomers, 3,6-dipropargyl-9-((±)-citronelly) carbazole, 3,6- dipropargyl y-9-(s-(-)-citronelly) carbazole, 3,6- dipropargyl -9-(2-ethylhexane) carbazole were also synthesized following the similar reaction protocol.

3,6-Dipropargyl-9-((±)-citronelly) carbazole

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.63(d, 2H, -Ar**H**); 7.29-7.28(d, 2H, -Ar**H**); 7.18-7.16(d, 2H, -Ar**H**); 4.8(d, 4H, -**CH2**CCH); 4.30-4.19(m, 2H, -N**CH2**); 2.54 (t, 2H, -C**CH**); 1.85-1.78

(m, 1H, -**CH**CH3); 1.39-1.08 (m, 8H, -**CH2** of C8 alkane functional group); 1.01 (d, 3H, -CH**CH3**); 0.86(d, 6H, -**CH3**).

3,6- Dipropargyl y-9-(s-(-)-citronelly) carbazole

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.63(d, 2H, -Ar**H**); 7.29-7.27(d, 2H, -Ar**H**); 7.18-7.15(dd, 2H, -Ar**H**); 4.8(d, 4H, -**CH2**CCH); 4.31-4.18(m, 2H, -N**CH2**); 2.54 (t, 2H, -C**CH**); 1.86-1.77 (m, 1H, -**CH**CH3); 1.55-1.44(m,1H, -**CH**CH3CH3); 1.39-1.07 (m, 8H, -**CH2** of C8 alkane functional group); 1.02(d, 3H, -CH**CH3**); 0.85(d, 6H, -**CH3**).

3,6- Dipropargyl -9-(2-ethylhexane) carbazole

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.62(d, 2H, -Ar**H**); 7.29-7.26(d, 2H, -Ar**H**); 7.17-7.14(dd, 2H, -Ar**H**); 4.8(d, 4H, -**CH2**CCH); 4.13-4.06(m, 2H, -N**CH2**); 2.54 (t, 2H, -C**CH**); 2.04-1.98 (m, 1H, -**CH**CH3); 1.41-1.21(m,8H, -**CH2** of 2-ethylhexyl group); 0.93-0.82(m, 6H, -**CH3**).

Synthesis of polymer

Polymer with C8-linear pendant unit

The donor containing linear polymer was synthesized by copper-catalyzed alkyne azide click reaction. In a long neck round bottom flask, 0.1gm (0.258 mmol) of dipropargyl carbazole and 63mg (0.258 mmol) of tetraethyleneglycol diazide were taken in 1.5ml of THF: CH_3CN (1:1) solvent combination. To this solution, 2mol% of CuI (1mg, 0.005mmol) and 8mg(0.058mmol) of N, N-diisopropylethylamine (DIPEA) were added. N_2 gas was purged for 10min; under N_2 sealed condition solution mixture was heated at 80°C for 5 days. After the polymerization was over, the solution was concentrated, and then the concentrated solution was in MeOH, and repeat the process for 4times. Finally, after drying a light orange color sticky polymer was recovered.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.78 (s, 2H, triazole -**CH**); 7.63 (d, 2H, Ar**H**); 7.22 (d, 2H, Ar**H**); 7.11 (d, 2H, Ar**H**); 5.26 (s, 4H, -O**CH2**, next to carbazole alkoxy); 4.45 (s, 4H, -**CH2** next to triazole from TEG segment); 4.15 (s, 2H, -N**CH2**); 3.78(t, 4H,-CH2**CH2**O of TEG segment); 3.50-3.48 (d, 8H, rest -**CH2** of TEG segment); 1.75 (s, 2H, -NCH2**CH2**); 1.24 (m, 10H, -**CH2** of pendant unit); 0.85-0.82 (t, 3H, -CH2**CH3**).

Using similar polymerization techniques all other polymers with different pendant units were synthesized.

Polymer with s- (-)-citronelly pendant unit

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.79 (s, 2H, triazole -**CH**); 7.62 (d, 2H, -Ar**H**); 7.23 (d, 2H, Ar**H**); 7.12 (d, 2H, Ar**H**); 5.25 (s, 4H, -O**CH2**, next to carbazole alkoxy); 4.46 (s, 4H, -**CH2** next to triazole from TEG segment); 4.17 (s, 2H, -N**CH2**); 3.78(t, 4H,-CH2**CH2**O of TEG segment); 3.50-3.45 (d, 8H, rest -**CH2** of TEG segment); 1.76 (m, 1H, -CH2**CH**CH3);1.49(m, 3H, -NCH2**CH2** and -**CH**CH3CH3); 1.30-1.09 (m, 6H, -**CH2** of pendant unit); 0.98(d, 3H, -CH**CH3**); 0.84(d, 6H, -CH**CH3CH3**).

Polymer with (±)-citronelly pendant unit

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.79 (s, 2H, triazole -**CH**); 7.62 (d, 2H, -Ar**H**); 7.23 (d, 2H, Ar**H**); 7.12 (d, 2H, Ar**H**); 5.25 (s, 4H, -O**CH2**, next to carbazole alkoxy); 4.46 (s, 4H, -**CH2** next to triazole from TEG segment); 4.16 (s, 2H, -N**CH2**); 3.77(t, 4H,-CH2**CH2**O of TEG segment); 3.49-3.44 (d, 8H, rest -**CH2** of TEG segment); 1.76 (m, 1H, -CH2**CH**CH3);1.51(m, 9H, -NCH2**CH2**, -**CH**CH3CH3 and 6H from -**CH2** of pendant unit); 0.98(d, 3H, -CH**CH3**); 0.84(d, 6H, -CH**CH3CH3**).

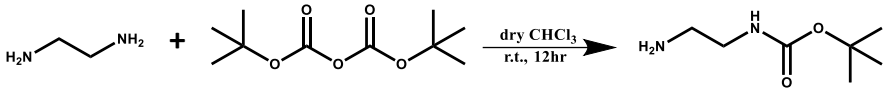
Polymer with 2-ethylhexyl pendant unit

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.80 (s, 2H, triazole -**CH**); 7.62 (d, 2H, -Ar**H**); 7.22 (d, 2H, Ar**H**); 7.11 (d, 2H, Ar**H**); 5.26 (s, 4H, -O**CH2**, next to carbazole alkoxy); 4.46 (s, 4H, -**CH2** next to triazole from TEG segment); 4.03 (s, 2H, -N**CH2**); 3.77(t, 4H,-CH2**CH2**O of TEG segment); 3.49-3.45 (d, 8H, rest -**CH2** of TEG segment); 1.96 (m, 1H, -**CH**CH2CH3); 1.31-1.24 (m, 8H, -**CH2** of pendant unit); 0.87-0.83 (m, 6H, -**CH3**).

Synthesis of folding agents

N-propyl-3,6-dinitronaphthalimide was synthesized following the procedure mentioned in the literature.[ref]

Tert-butyl (2-aminoethyl) carbamate



The monoprotected primary amine was synthesized by adding di-*tert*-butyl pyrocarbonate (Boc anhydride) (2.14 gm, 9.784mmol) in a $CHCl_3$ (dry) solution containing 1,2-ethylenediamine (5.88gm, 97.84 mmol). The solution was stirred at room temperature for 12hr which resulted in a solid precipitate. Solid was filtered off and the organic layer was extracted with brine

solution. The organic layer was passed through Na_2SO_4 and after removing the solvent under reduced pressure a colorless viscous liquid was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 4.91 (s, 1H, -**NH**); 3.16-3.13 (q, 2H, -**CH2**NH); 2.79-2.76 (t, 2H, -**CH2**NH2); 1.43 (s, 9H, -**CH3**); 1.16 (s, 2H, -**NH2**).

Using similar synthetic strategies other monoprotected primary amines were synthesized.

Tert-butyl (3-aminopropyl) carbamate

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 4.91 (s, 1H, -**NH**); 3.24-3.16 (q, 2H, -**CH2**NH); 2.78-2.75 (t, 2H, -**CH2**NH2); 1.65-1.58(m, 2H, -**CH2**CH2NH2); 1.44 (s, 9H, -**CH3**).

Tert-butyl (4-aminobutyl) carbamate

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 4.67 (s, 1H, -**NH**); 3.14-3.11(q, 2H, -**CH2**NH); 2.73-2.70 (t, 2H, -**CH2**NH2); 1.56-1.40(m, 13H, 4H of -**CH2CH2**CH2NH2 and 9H from -**CH3**).

3,6-Dinitronapthaliimide with Boc-protected C2 spacer

In a 100ml Rb, 1gm (3.47mmol) of 3,6-dinitronaphthalic anhydride and 0.68gm (4.25mmol) of tert-butyl(2-aminoethyl) carbamate were taken in 50ml of absolute EtOH and refluxed the mixture for 12 hr under N_2 atmosphere. From an initial wine-red solution, a solid precipitate was observed when the temperature was raised to reflux temperature. Obtained solid was separated, rinsed multiple times with absolute EtOH, and dried thoroughly to recover a brown color solid product.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.47 (d, 2H, Ar**H**); 9.32 (d, 2H, Ar**H**); 4.83 (s, 1H, -**NH**); 4.41 (t, 2H, -N**CH2**CH2); 3.58 (d, 2H, -NCH2**CH2**NH); 1.18 (s, 9H, -**CH3**).

Similarly, all other Boc-protected folding agents were synthesized.

3,6-Dinitronapthaliimide with Boc-protected C3 spacer

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.47 (d, 2H, Ar**H**); 9.34 (d, 2H, Ar**H**); 5.03 (s, 1H, -**NH**); 4.31 (t, 2H, -N**CH2**CH2); 3.22-3.17 (m, 2H, -NCH2**CH2**NH); 1.98-1.95(t, 2H, -CH2**CH2**CH2); 1.45 (s, 9H, -**CH3**).

3,6-Dinitronapthaliimide with Boc-protected C4 spacer

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.46 (d, 2H, Ar**H**); 9.33 (d, 2H, Ar**H**); 4.6 (s, 1H, -**NH**); 4.24 (t, 2H, -N**CH2**CH2); 3.21 (m, 2H, -NCH2**CH2**NH); 1.81-1.77(t, 2H, -CH2CH2**CH2**CH2NH); 1.64-1.61(t,2H, -CH2**CH2**CH2CH2NH); 1.42 (s, 9H, -**CH3**).

C2 spacer folding agent with perchlorate ammonium salt

The Boc-protected C2 spacer naphthaliimide (0.45gm, 1.05mmol) was taken in 20ml of dry CHCl3 and 10 equivalent (0.38ml) of aqueous $HClO_4$ was added to the solution. The solution was stirred at room temperature for 6hr. Resulted precipitate was isolated and rinsed twice with CHCl3 and then twice with absolute EtOH. After drying thoroughly, a pinkish solid was recovered.

^{1}H-NMR (400 MHz, DMSO-d6, δ ppm): 9.81 (d, 2H, Ar**H**); 9.11 (d, 2H, Ar**H**); 7.8 (s, 3H, -N**H3**); 4.36 (t, 2H, -N**CH2**); 3.18 (sextet, 2H, -CH2**CH2**NH3; splitting of this proton changed to triplet on D_2O exchange).

Other quaternary ammonium salt-based folding agents were also synthesized using a similar synthetic protocol.

C3 spacer folding agent with perchlorate ammonium salt

^{1}H-NMR (400 MHz, DMSO-d6, δ ppm): 9.80 (d, 2H, Ar**H**); 9.08 (d, 2H, Ar**H**); 7.69 (s, 3H, -N**H3**); 4.15 (t, 2H, -N**CH2**); 2.95 (sextet, 2H, -CH2**CH2**NH3); 1.98(t, 2H, -**CH2**CH2NH3).

C4 spacer folding agent with perchlorate ammonium salt

^{1}H-NMR (400 MHz, DMSO-d6, δ ppm): 9.81 (d, 2H, Ar**H**); 9.09 (d, 2H, Ar**H**); 7.62 (s, 3H, -N**H3**); 4.12 (t, 2H, -N**CH2**); 2.86 (sextet, 2H, -CH2**CH2**NH3); 1.75(t, 2H, -**CH2**CH2NH3); 1.64(t, 2H, -**CH2**CH2CH2NH3).

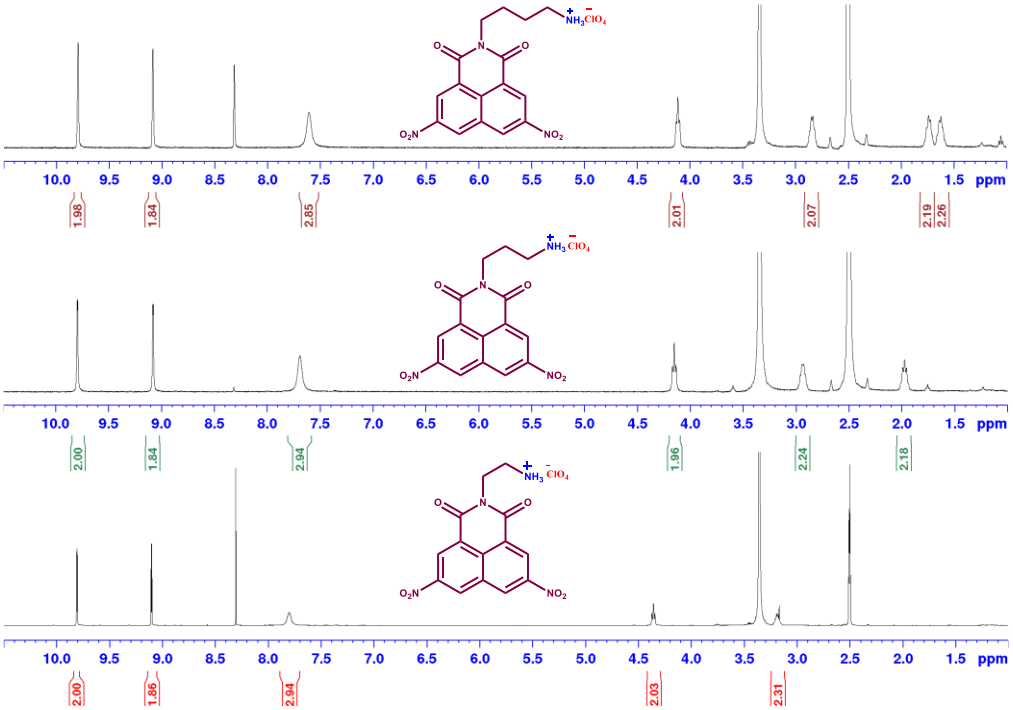


Figure S1: *[1]H-NMR stacked plots of acceptor folding agent containing ammonium perchlorate salt with varying spacer length.*

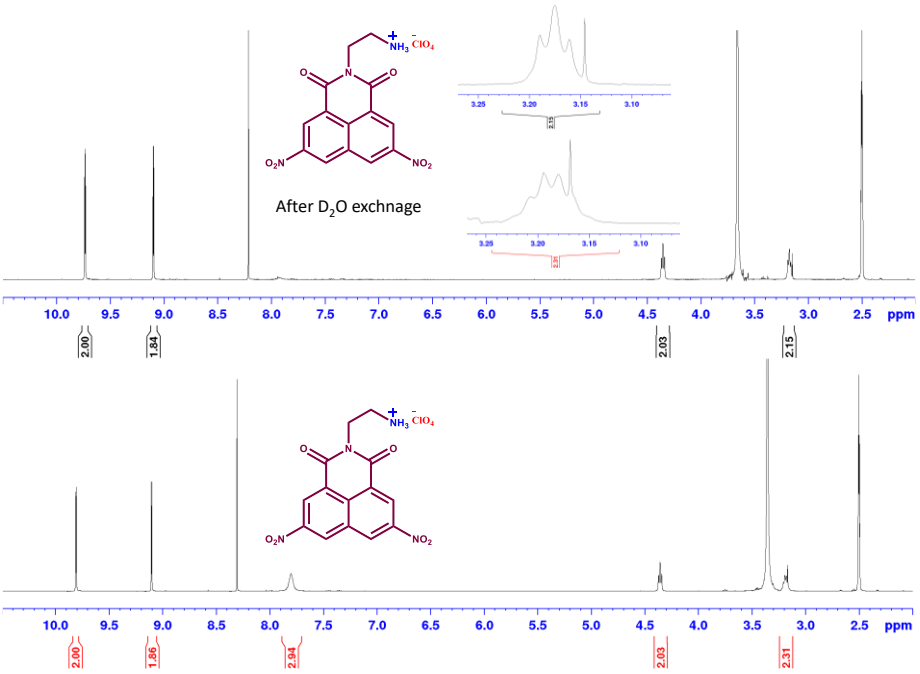


Figure S2: *[1]H-NMR stacked plots of C_2 spacer folding agent containing ammonium perchlorate salt recorded in DMSO-d6 solvent. The formation of ammonium salt was confirmed by the D_2O exchange experiment. The methylene protons adjacent to the ammonium group appeared as a multiplet, however upon carrying out D_2O exchange, it collapsed into a clean triplet. This confirmed that the multiplet was due to coupling with the ammonium protons.*

Synthesis of tetraethyleneglycol (TEG) diazide

Synthesis of TEG ditosylate

In a THF solution, 10gm (51.49mmol) of TEG and 6.18gm (154.47mmol) of NaOH were taken and 5ml of water was added to it. The solution mixture was stirred for 15 minutes under ice-cold conditions and then 29.45 gm (154.47mmol) of tosylchloride was dropwise added; and stirred at room temperature for 12hr. THF was evaporated under reduced pressure; H_2O was added, and the product was extracted in $CHCl_3$. The organic layer was passed through Na_2SO_4 and finally after drying a very dense liquid was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.79 (d, 4H, Ar**H**); 7.34-7.32(d, 4H, Ar**H**); 4.14 (t, 4H, -**CH$_2$**OSO_2ArHCH_3); 3.66 (m, 4H, -O**CH$_2$**); 3.55 (8H, -**CH$_2$** of TEG skeleton); 2.43 (s, 6H, -OSO_2ArH**CH$_3$**).

Synthesis of TEG diazide

TEG-ditosylate (27.17gm, 54.06mmol) was taken in 150ml of CH_3CN and 10 equivalent (35.14gm, 540.6mmol) of NaN_3 was added. The solution was refluxed for 3 days under N_2 atmosphere. The solvent was evaporated under reduced pressure and H_2O was added to the residue. The product was extracted in $CHCl_3$, and the organic layer was passed through Na_2SO_4. Finally, after drying a viscous liquid was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 3.67 (12H, -**CH$_2$** of TEG skeleton); 3.38 (t, 4H, -**CH$_2$**N_3).

NMR titration experiments – effect of lateral N-alkyl substituent

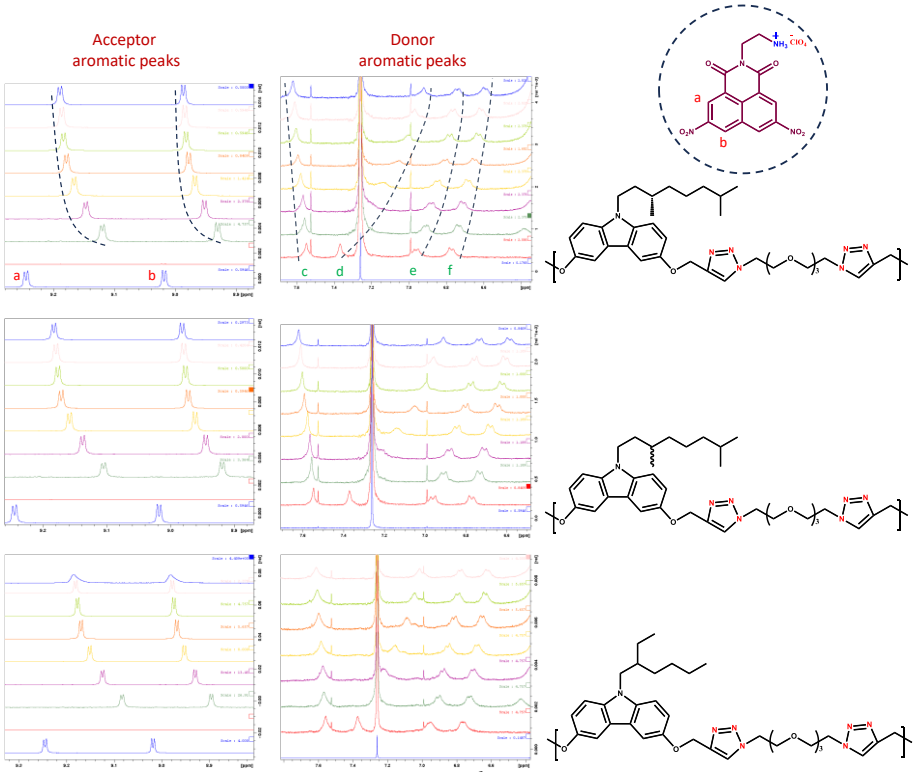


Figure S3: *Variation in the aromatic region of the ^{1}H-NMR spectra of the polymer as a function of increasing amount of acceptor containing folding agent, NMI(NO$_2$)$_2$-C$_2$-NH$_3^+$ClO$_4^-$. The measurements were performed in a mixture of CDCl$_3$:CH$_3$CN (1:2) solvent.*

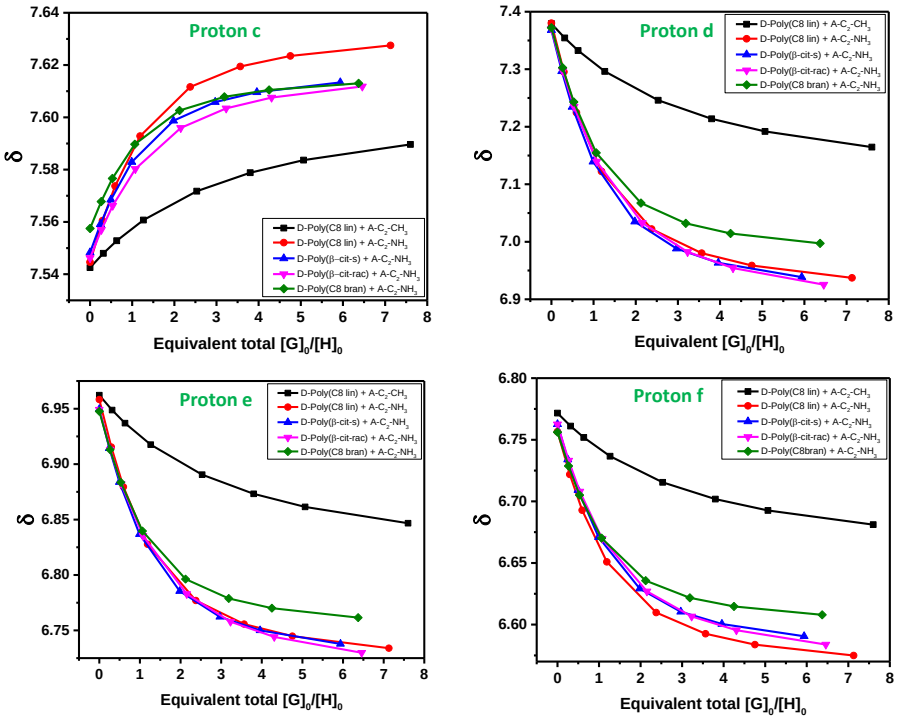


Figure S4: *Change in chemical shift of carbazole aromatic protons peaks as a function of increasing amount of the folding agent with a C2 spacer, namely NMI(NO$_2$)$_2$-C$_2$-NH$_3^+$, and with the model folding agent without the ammonium unit, namely NMI(NO$_2$)$_2$-C$_2$-CH$_3$. It is evident that the extent of shift is much smaller in the case of the later, suggesting a weaker interaction.*

Effect of folding agent spacer length-NMR titration experiments

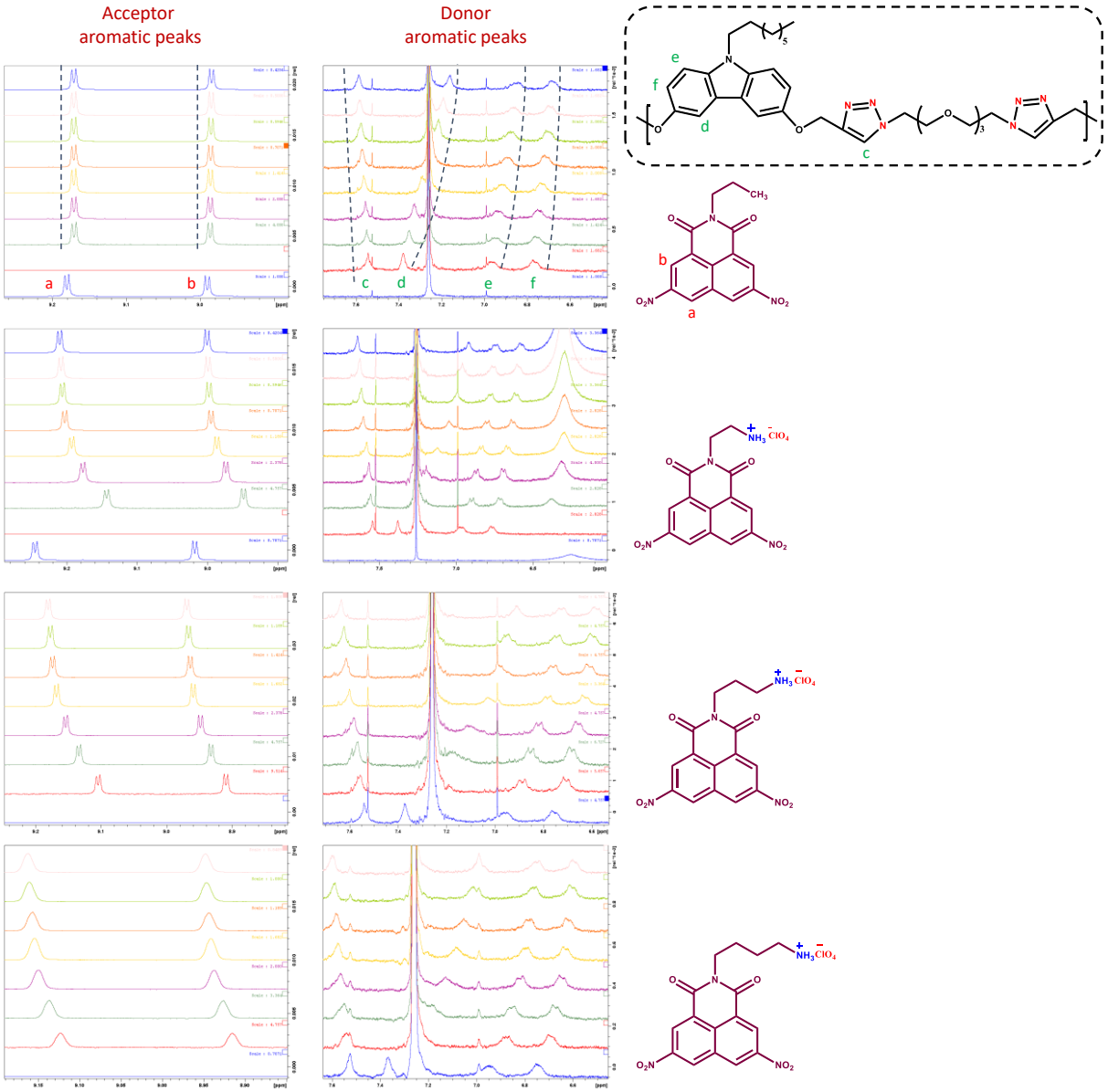


Figure S5: *Change in the chemical shift of carbazole and folding agent's aromatic peaks as a function of an increasing amount of acceptor folding agent having different spacer lengths. The measurements were performed in a mixture of $CDCl_3$:CH_3CN (1:2) solvent.*

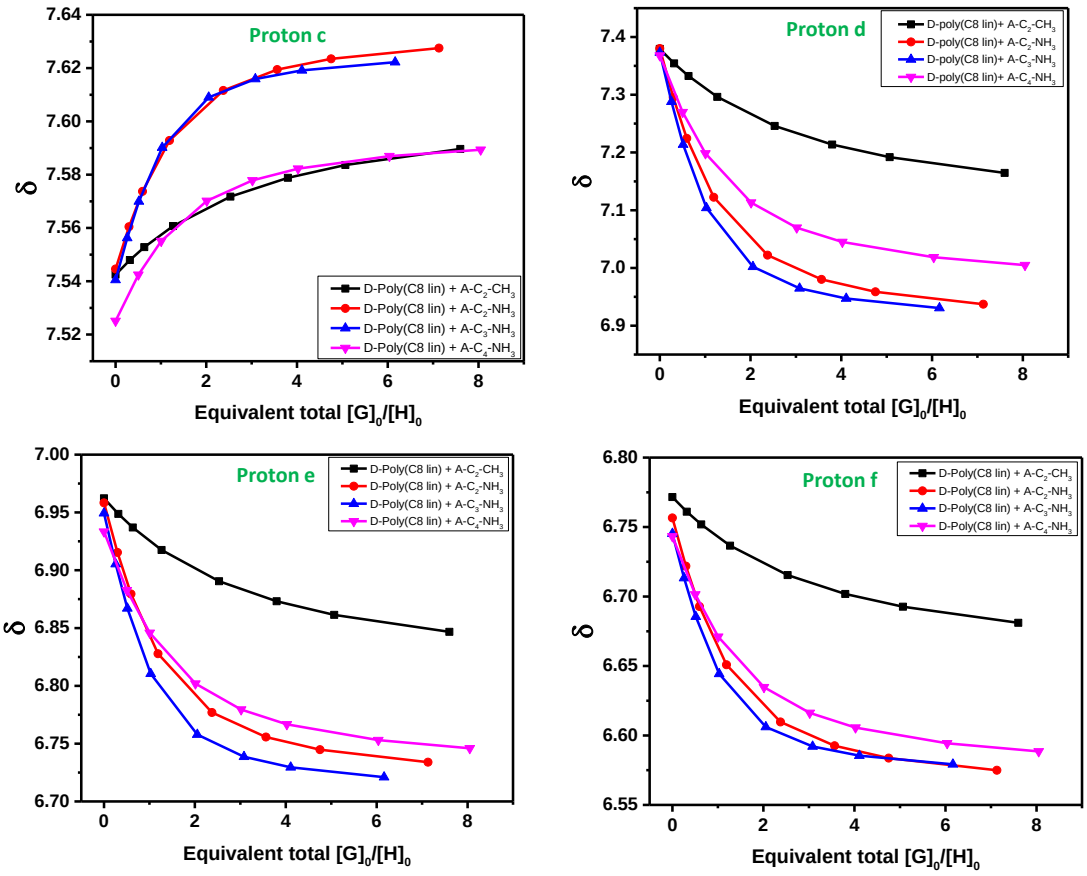


Figure S6: *Variation of the chemical shift of aromatic peaks from carbazole and various folding agents with different spacer lengths as a function of increasing amount of folding agent.*

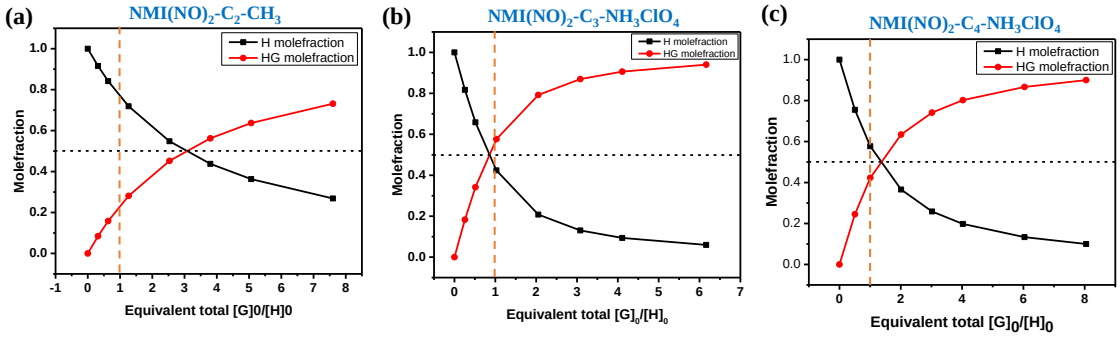


Figure S7: *The quality of fitting and change in the mole fraction of free polymer to the complexed fraction with an increasing amount of added external folding agent obtained from NMR titration experiments.*

Estimation of association constant-UV-Visible spectral titration experiments

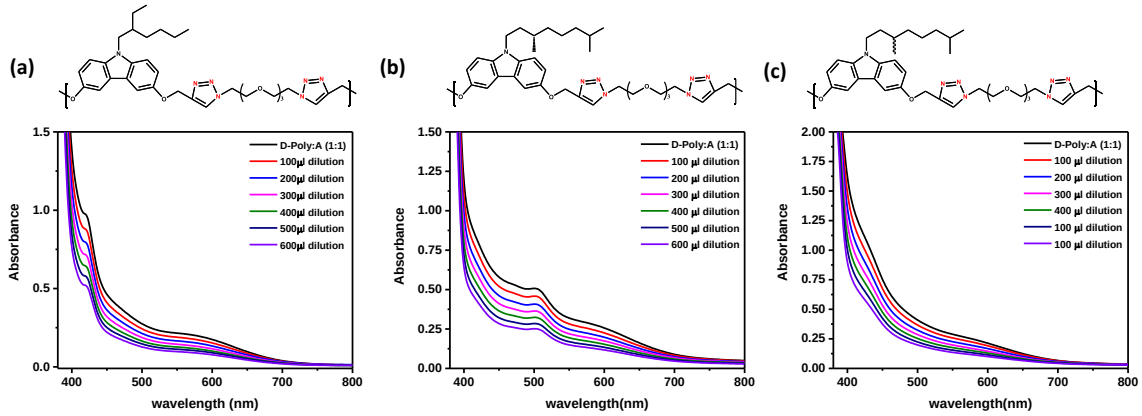


Figure S8: *Variation of CT band intensity of different polymers upon serial dilution with acceptor folding agent, $NMI(NO_2)_2$-C_3-$NH_3^+ClO_4^-$. The measurements were performed in a mixture of $CHCl_3$:CH_3CN (1:2) solvents.*

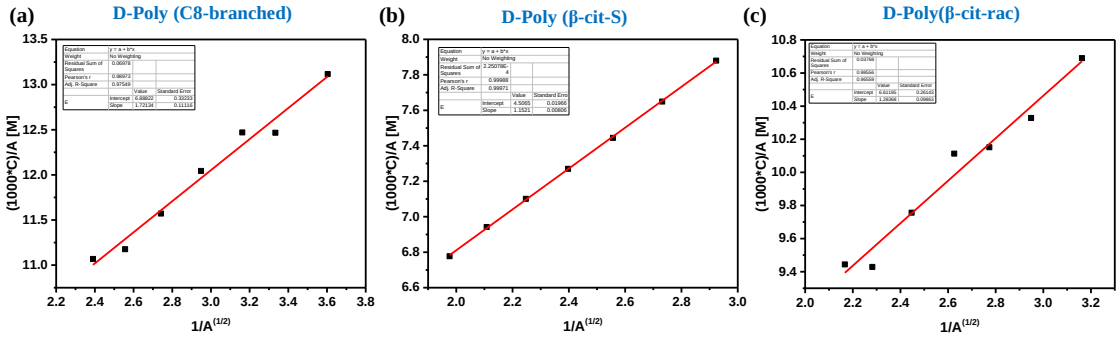


Figure S9: *Fitted Benesi-Hildabrand plots[2] obtained from the variation of CT band intensity with concentration of the solution, upon a serial dilution, during UV-visible titration experiments in the presence of an external folding agent, $NMI(NO_2)_2$-C_3-$NH3^+ClO_4^-$.*

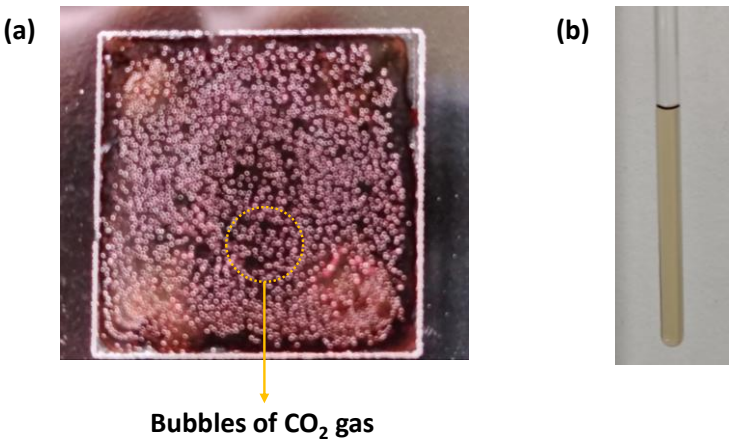


Figure S10: *(a) The effervescence of CO_2 gas, due to neutralization of ammonium functional group with aqueous $NaHCO_3$ solution. (b) Brownish colour solution obtained by dissolving the merlot colour film in $CDCl_3$ and CH_3CN (1:2) solvent mixture.*

References:

1. J. B. Harlé, S. Mine, T. Kamegawa, V. T. Nguyen, T. Maeda, H. Nakazumi and H. Fujiwara, *J. Phys. Chem. C*, 2017, **121**, 15049–15062.
2. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.,* 1949, **71**, 2703–2707.