Electronic Supplementary Information

Self-assembly of fluorescentdiimidazolium salts: tailor properties of the aggregates changing alkyl chain features

FlorianaBilleci, Francesca D'Anna,* Salvatore Marullo, Renato Noto

Synthesis of *N,N'*-bis-(3-imidazol-yl-propyl)naphthalene-diimide.

1,4,5,8-naphthalenetetracarboxylic dianhydride (1.00 g; $3.73 \cdot 10^{-3}$mol) was dissolved in 12.5 mL of anhydrous DMF, and the solution obtained was heated at 80 °C. Into a two-neck flask, 1-(3-aminopropyl)imidazole (1.026 g; $8.21 \cdot 10^{-3}$mol) was dissolved in 12.5 mL of anhydrous DMF and obtained solution was heated at 140 °C.

The solution of 1,4,5,8-naphthalenetetracarboxylic dianhydride was added to the 1-(3-aminopropyl)imidazole solution. The mixture was stirred at 140 °C for 24 hours.

The resulting mixture was allowed to cool down, poured in water/acetone (3/1; 30 mL) mixture, then in cold diethyl ether. Stirring for 30 minutes afforded a dark precipitate. The solid was filtered off in vacuo and thoroughly washed with diethyl ether and small amounts of ethanol.

Yield: 70%; dark solid.^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 8.63 (s, 4H); 7.66 (s, 2H); 7.21 (s, 2H); 6.87 (s, 2H); 4.10 (m, 8H); 2.13 (m, 4H).

General synthesis of *N,N'*-bis-(1-alkyl-3-propylimidazolium)naphthalene-diimidediiodide salts.

N,N'-bis-(3-imidazol-yl-propyl)naphthalene-diimide (0.25 g; $5.19 \cdot 10^{-4}$mol) was dissolved in 10 mL of anhydrous DMF, and solution obtained was heated at 80 °C. Into a two-neck flask, the suitable alkyl iodide ($1.14 \cdot 10^{-3}$mol) was dissolved in 10 mL of anhydrous DMF; the solution was then heated at 90 °C.

The solution of *N,N'*-bis-(3-imidazol-yl-propyl)naphthalene-diimide was added to the alkyl iodide solution. The mixture was stirred at 90 °C for 72 hours.

The solvent was removed in vacuo and the dark solid obtained was washed with diethyl ether (20 mL), with ultrasounds irradiation until a colourless organic phase was obtained. Finally, the dark solid was washed with refluxing ethyl acetate (50 mL) overnight.

***N,N'*-bis-(1-hexyl-3-propylimidazolium)naphthalene-diimidediiodide [C_6NDI][I].**

Yield: 90%; dark solid; m. p.: 170.8 °C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.21 (s, 2H); 8.70 (s, 4H); 7.83 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.28 (m, 4H), 1.79 (m, 4H), 1.27 (bs, 12H), 0.86 (m, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6); δ (ppm): 163.3; 136.6; 130.9; 126.9; 122.9; 49.4; 47.5; 31.0; 29.7; 28.6; 25.5; 22.3; 14.2.HRMS calcd. for $C_{38}H_{48}N_6O_4$ 326.1863, found 326.1899.

***N,N'*-bis-(1-heptyl-3-propylimidazolium)naphthalene-diimmidediiodide [C_7NDI][I].**

Yield: 87%; dark solid; m. p.: 170.1°C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.25 (s, 2H); 8.70 (s, 4H); 7.83 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.27 (m, 4H); 1.79 (m, 4H); 1.25 (m, 16H); 0.84 (t, J = 4.0 Hz, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6); δ (ppm): 163.3; 136.6; 130.9; 126.9; 126.7; 122.9; 31.7; 29.4; 25.9; 22.5; 14.4.HRMS calcd. for $C_{40}H_{52}N_6O_4$ 340.2019, found 340.2057.

***N,N′*-bis-(1-octyl-3-propylimidazolium)naphthalene-diimidediiodide [C_8NDI][I].**

Yield: 83%; dark solid; m. p.: 146.9 °C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.21 (s, 2H); 8.70 (s, 4H); 7.83 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.28 (m, 4H); 1.80 (m, 4H); 1.25 (m, 20H); 0.84 (m, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6); δ (ppm): 163.3; 130.9; 130.8; 126.9; 123.0; 122.9; 49.4; 47.4; 31.6; 31.4; 29.7; 28.9; 25.9; 22.4; 14.3.HRMS calcd. for $C_{42}H_{56}N_6O_4$ 354.2176, found 354.2213.

***N,N′*-bis-(1-nonyl-3-propylimidazolium)naphthalene-diimidediiodide [C_9NDI][I].**

Yield: 85%; dark solid; m. p.: 200.2°C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.21 (s, 2H); 8.70 (s, 4H); 7.83 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.28 (m, 4H); 1.79 (s, 4H); 1.24 (m, 24H); 0.83 (m, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6); δ (ppm): 163.3; 136.6; 130.9; 126.9; 122.9; 49.3; 37.6; 31.7; 30.6; 29.8; 29.0; 25.9; 22.5; 14.4.HRMS calcd. for $C_{44}H_{60}N_6O_4$ 368.2332, found 368.2337.

***N,N′*-bis-(1-decyl-3-propylimidazolium)naphthalene-diimidediiodide [C_{10}NDI][I].**

Yield: 85%; dark solid; m. p.: 104.0 – 106.8 °C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.22 (s, 2H); 8.70 (s, 4H); 7.84 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.27 (m, 4H); 1.79 (m, 4H); 1.22 (m, 28H); 0.83 (m, 6H). ^{13}C-NMR (300 MHz, DMSO-d_6); δ (ppm): 163.4; 136.6; 130.9; 126.9; 126.7; 122.9; 55.5; 49.4; 47.4; 37.7; 34.8; 31.7; 29.8; 29.4; 29.3; 29.1; 28.8; 25.9; 22.5; 14.4.HRMS calcd. for $C_{44}H_{60}N_6O_4$ 382.2489, found 382.2500

***N,N′*-bis-(1-propyl-3-undecylimidazolium)naphthalene-diimidediiodide [C_{11}NDI][I].**

Yield: 88%; dark solid; m. p.: 202.6 °C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.21 (s, 2H); 8.70 (s, 4H); 7.83 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.27 (m, 4H); 1.79 (m, 4H); 1.22 (m, 32H); 0.83 (m, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6); δ (ppm): 163.3; 136.6; 130.9; 126.9; 126.7; 122.9; 49.4; 47.4; 46.6; 37.6; 34.9; 31.7; 29.7; 29.4; 29.2; 29.1; 28.8; 28.5; 25.9; 22.5; 14.4.HRMS calcd. for $C_{46}H_{64}N_6O_4$ 396.2645, found 396.2656.

***N,N′*-bis-(1-dodecyl-3-propylimidazolium)naphthalene-diimidediiodide [C_{12}NDI][I].**

Yield: 88%; dark solid; m. p.: 144.0°C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.22 (s, 2H); 8.70 (s, 4H); 7.84 (d, J = 8.0 Hz, 4H); 4.32 (m, 5H); 4.17 (m, 7H); 2.27 (m, 4H); 1.79 (s, 4H); 1.20 (m, 36H); 0.83 (m, 6H). ^{13}C-NMR (400 MHz, DMSO-d_6); δ (ppm): 163.3; 156.1; 136.6; 131.1; 130.9; 129.8; 126.9; 122.9; 108.2; 49.4; 47.4; 31.4; 29.8; 28.5; 25.9; 24.5; 22.4; 14.3; 9.1.HRMS calcd. for $C_{48}H_{68}N_6O_4$ 410.2802, found 410.2813.

Synthesis of*N,N′*-bis-[1-propyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium]-naphthalene-diimidediiodide [C_8FNDI][I].

N,N'-bis-(3-imidazol-yl-propyl)naphthalene-diimide (0.100 g; $2.075 \cdot 10^{-4}$mol) was dissolved in 5 mL of anhydrous DMF, and the solution obtained was heated at 80 °C. Into a two-neck flask, 1,1,2,2-tetrahydroperfluorooctiliodide (0.216 g; $4.56 \cdot 10^{-4}$mol) was dissolved in 5 mL of anhydrous DMF; the solution was heated at 80 °C. The solution of *N,N'*-bis-(3-imidazol-yl-propyl)naphthalene-diimide was added to the solution of alkyl iodide. The mixture was stirred, under argon atmosphere at 80 °C for 4 days.

The solvent was removed in vacuo and the dark solid obtained was washed with diethyl ether (20 mL), with ultrasounds irradiation until a colourless organic phase was obtained. Finally, the dark solid was washed with refluxing ethyl acetate (50 mL) overnight.

Yield: 81%; dark solid; m. p.: 179.2 °C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.30 (s, 2H); 8.86-8.71 (m, 6H); 7.91-7.54 (m, 8H); 4.59 (m, 2H); 4.37 (m, 5H); 4.15 (m, 5H); 2.27 (m, 8H).

HRMS calcd. for $C_{42}H_{30}F_{26}N_6O_4$ 588.0951, found 588.0945.

Synthesis of *N,N′*-bis-[1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-enicosafluorododecyl)-3-propylimidazolium]-naphthalene-diimidediiodide [C_{12}FNDI][I].

N,N'-bis-(3-imidazol-yl-propyl)naphthalene-diimide (0.100 g; $2.075 \cdot 10^{-4}$mol) was dissolved in 5 mL of anhydrous DMF and the solution obtained was heated at 80 °C. Into a two-neck flask, 1,1,2,2-tetrahydroperfluorododecyliodide (0.31 g; $4.56 \cdot 10^{-4}$mol) was dissolved in 5 mL of anhydrous DMF; the solution was heated at 120 °C.

The solution of *N,N'*-bis-(3-imidazol-yl-propyl)naphthalene-diimide was added to the solution of alkyl iodide. The mixture obtained was stirred, under argon atmosphere, at 120 °C for 4 days.

The solvent was removed in vacuo and the dark solid obtained was washed with diethyl ether (20 mL) with ultrasounds irradiation until a colourless organic phase was obtained. Finally, the dark solid was washed with refluxing ethyl acetate (50 mL) overnight.

Yield: 50%; dark solid; m. p.: 182.2 °C. ^{1}H-NMR (400 MHz, DMSO-d_6); δ (ppm): 9.30 (s, 2H); 8.87-8.70 (m, 6H); 7.92-7.56 (m, 8H); 4.58 (m, 2H); 4.30 (m, 5H); 4.11 (m, 5H); 2.25 (m, 8H).

HRMS calcd. for $C_{50}H_{30}F_{42}N_6O_4$ 788.0902, found 788.0823.

Determination of thermodynamic parameters from temperature dependent measurements

To determine the thermodynamic parameters we used the procedure reported by Meijer et al.[1]

To this aim, we first calculated the number averaged degree of polymerization at each temperature DP_n (T) by means of equation (1).

$$DP_n(T) = \frac{1}{\sqrt{1 - \alpha_{agg}(T)}} \qquad (1)$$

At a given temperature DP_n is related to the association constant K_{ass} by equation (2), rearrangement of which yields K_{ass} as expressed by equation (3), where C_T is the total concentration of salt.

$$DP_n(T) = \frac{1}{2} + \frac{1}{2}\sqrt{4 \cdot K_{ass}(T) \cdot C_T + 1} \qquad (2)$$

$$K_{ass} = \frac{[(2 \cdot DP_n(T) - 1)^2 - 1]}{4 \cdot C_T} \qquad (3)$$

[1] M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F. A. de Greef, P. van der Schoot, A. P. H. J. Schenning, E. W. Meijer, *Chem. Eur. J.* **2010**, *16*, 362-367.

Table S1. Melting temperatures, enthalpy and entropy values determined by DSC measurements.

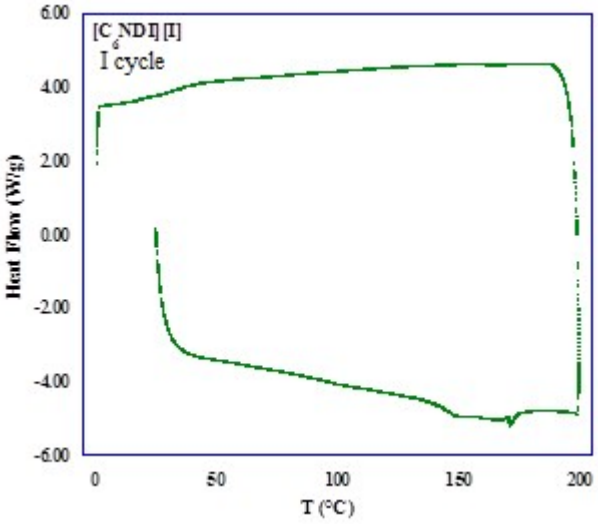
Salt	T_m (°C)	ΔH_m (J/mol)	ΔS_m (J/K mol)
[C_6NDI][I]	170.8	316	1.0
[C_7NDI][I]	170.1	4000	9.0
[C_8NDI][I]	146.9	792	2.0
[C_9NDI][I]	200.2	1344	3.0
[C_{10}NDI][I]	-	-	-
[C_{11}NDI][I]	202.6	1420	3.0
[C_{12}NDI][I]	144.0	4600	11.0
[C_8FNDI][I]	179.2	3440	8.0
[C_{12}FNDI][I]	182.2	4920	11.0

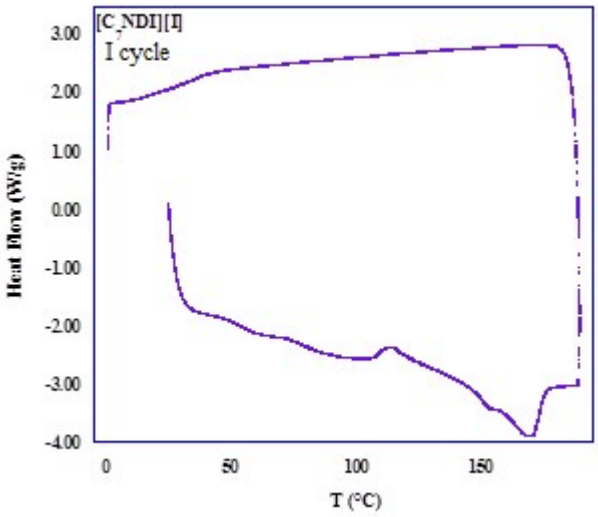
Table S2. Salts concentration corresponding to the onset of aggregation (C_{on}) for [CnNDI][I] salts as a function of solvent.

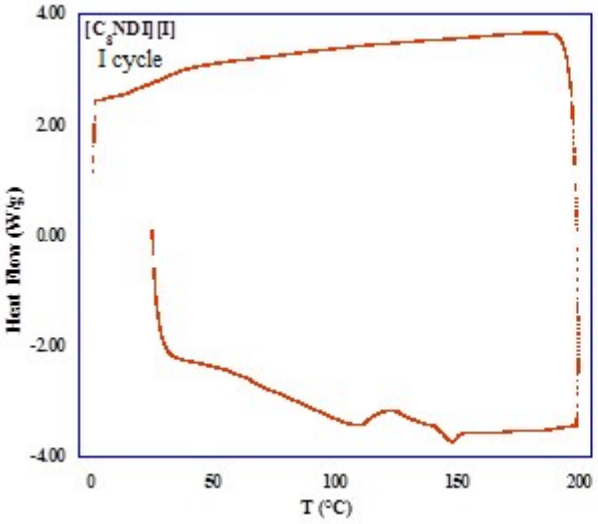
Salt	$10^6 \cdot C_{on,THF}$ □□M□	$10^6 \cdot C_{on,DMF}$ □□M□	$10^6 \cdot C_{onCHCl3}$ □□M□	$10^6 \cdot C_{on,1,4\text{-}Diox}$ □□M□
[C_6NDI][I]	2.6	2.3		
[C_7NDI][I]	5.5	1.8		
[C_8NDI][I]	3.1	1.1		
[C_9NDI][I]	2.4	2.0		
[C_{10}NDI][I]	3.3	1.9		
[C_{11}NDI][I]	1.9	1.3		
[C_{12}NDI][I]	1.0	2.4	3.0	2.6
[C_8FNDI][I]		2.7		
[C_{12}FNDI][I]		3.3		

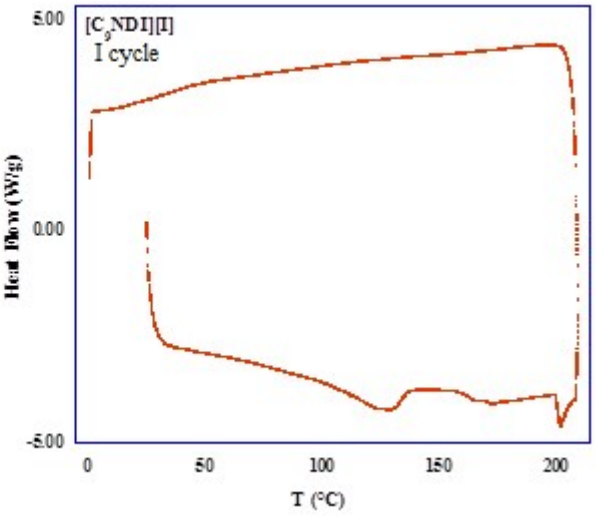
Table S3. Position of main emission band (λ_{max}) in solution and in solid state as a function of alkyl chain and solvent.

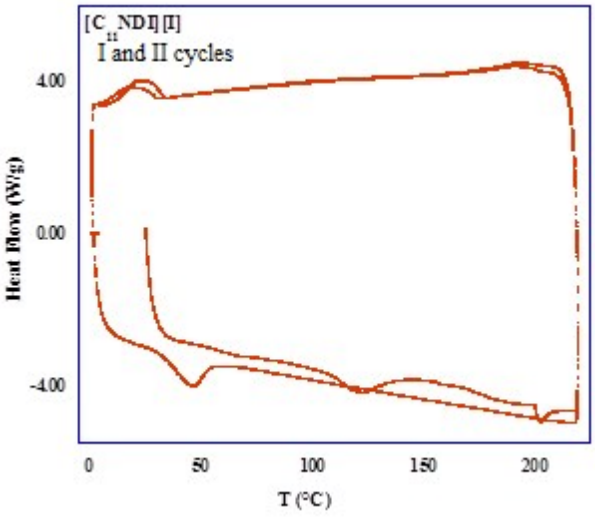
	λ_{max} (nm)							
	THF		**DMF**		**$CHCl_3$**		**1,4-dioxane**	
Salt	**Solid state**	**Solution**	**Solid state**	**Solution**	**Solid state**	**Solution**	**Solid state**	**Solution**
[C_6NDI][I]	376	410						
[C_7NDI][I]	375	408						
[C_8NDI][I]	375	408						
[C_9NDI][I]	375	393						
[C_{10}NDI][I]	375	408						
[C_{11}NDI][I]	375	408						
[C_{12}NDI][I]	375	410	375	419	375	410	376	420

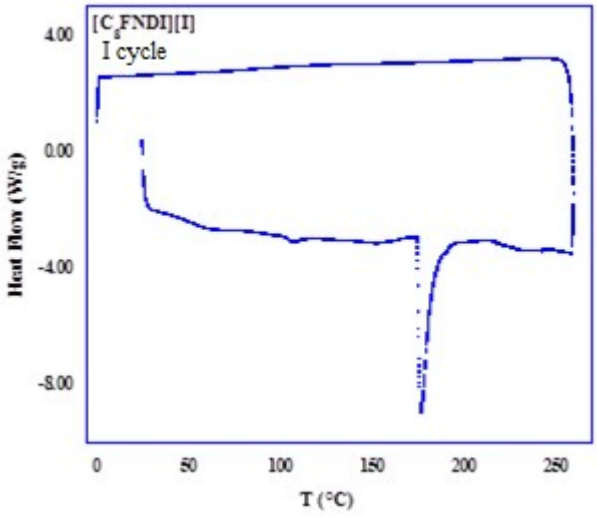

[C6NDI][I]
I cycle
Heat Flow (W/g)
T (°C)


[C7NDI][I]
I cycle
Heat Flow (W/g)
T (°C)


[C8NDI][I]
I cycle
Heat Flow (W/g)
T (°C)


[C9NDI][I]
I cycle
Heat Flow (W/g)
T (°C)


[C11NDI][I]
I and II cycles
Heat Flow (W/g)
T (°C)


[C8FNDI][I]
I cycle
Heat Flow (W/g)
T (°C)

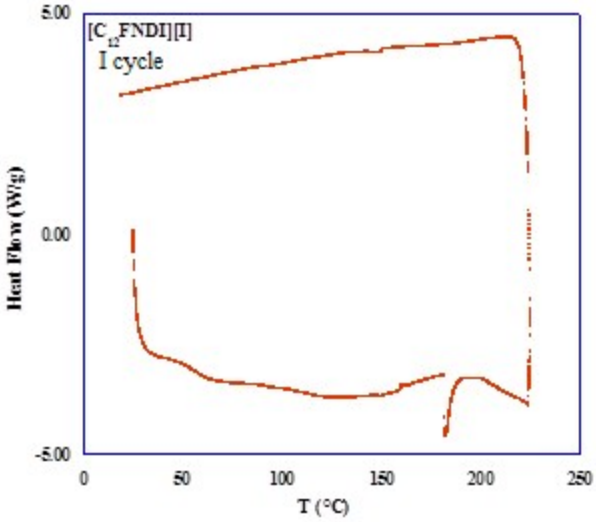
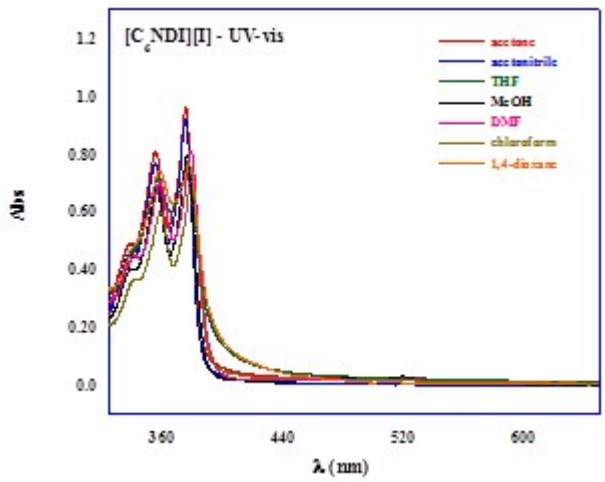
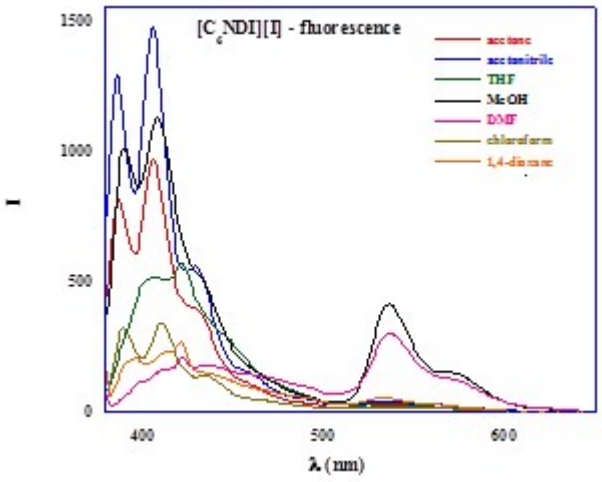
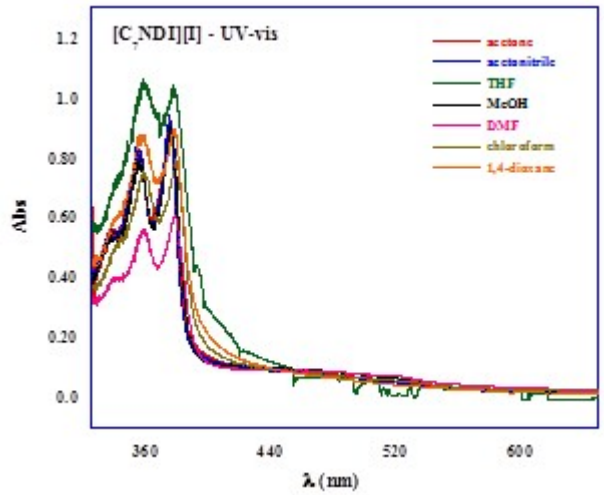
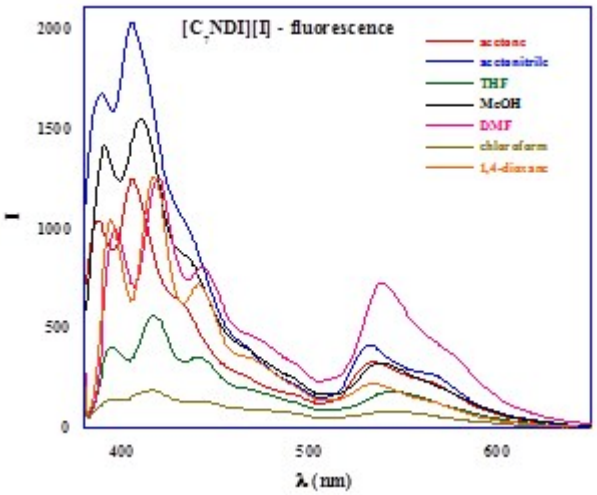


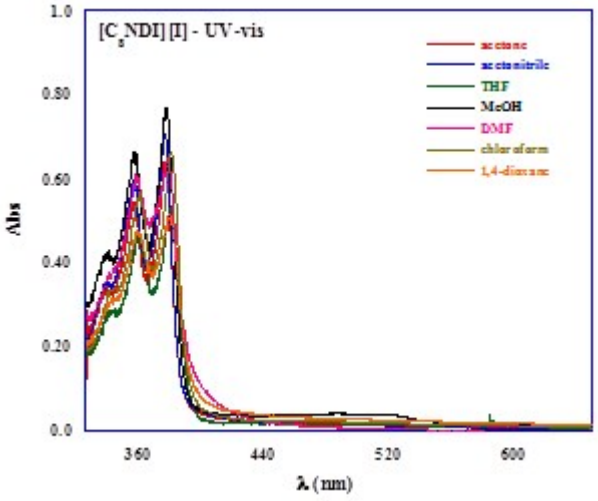
Figure S1. DSC thermograms of the synthesized salts.

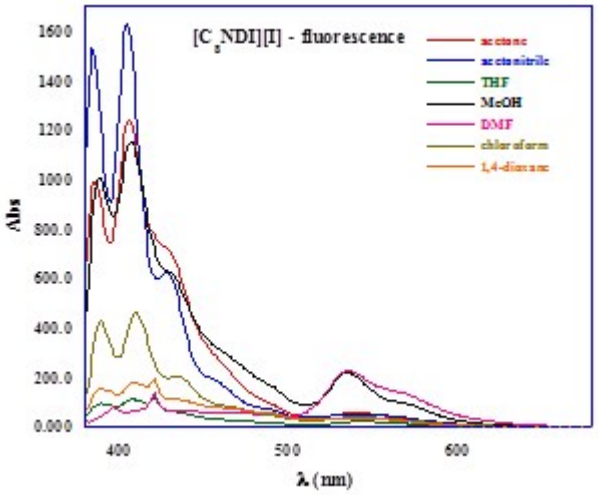


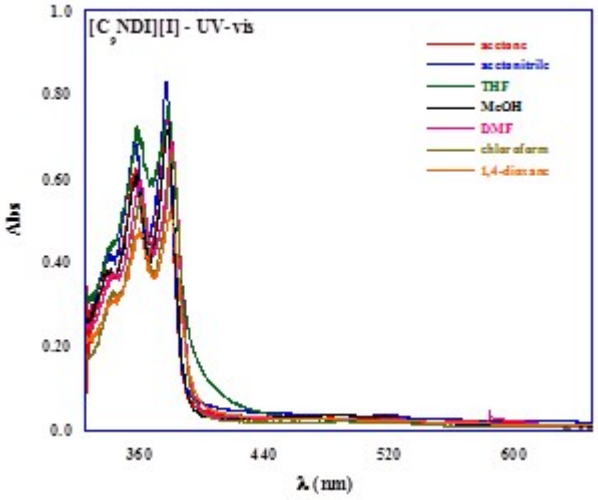


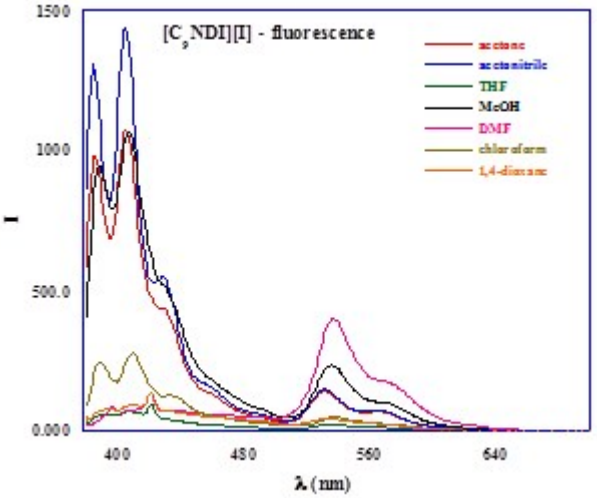


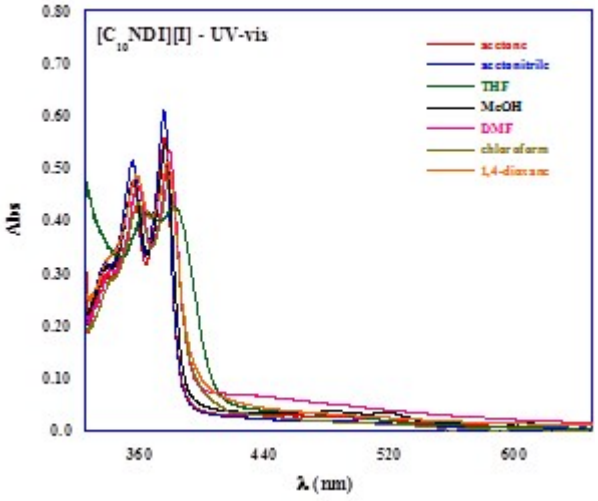


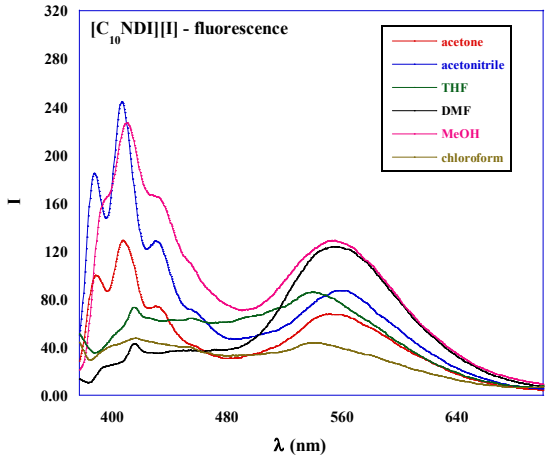

[C8NDI][I] - UV-vis
acetone
acetonitrile
THF
MeOH
DMF
chloroform
1,4-dioxane
Abs
λ (nm)


[C8NDI][I] - fluorescence
acetone
acetonitrile
THF
MeOH
DMF
chloroform
1,4-dioxane
Abs
λ (nm)


[C9NDI][I] - UV-vis
acetone
acetonitrile
THF
MeOH
DMF
chloroform
1,4-dioxane
Abs
λ (nm)


[C9NDI][I] - fluorescence
acetone
acetonitrile
THF
MeOH
DMF
chloroform
1,4-dioxane
I
λ (nm)


[C10NDI][I] - UV-vis
acetone
acetonitrile
THF
MeOH
DMF
chloroform
1,4-dioxane
Abs
λ (nm)


[C10NDI][I] - fluorescence
acetone
acetonitrile
THF
DMF
MeOH
chloroform
I
λ (nm)

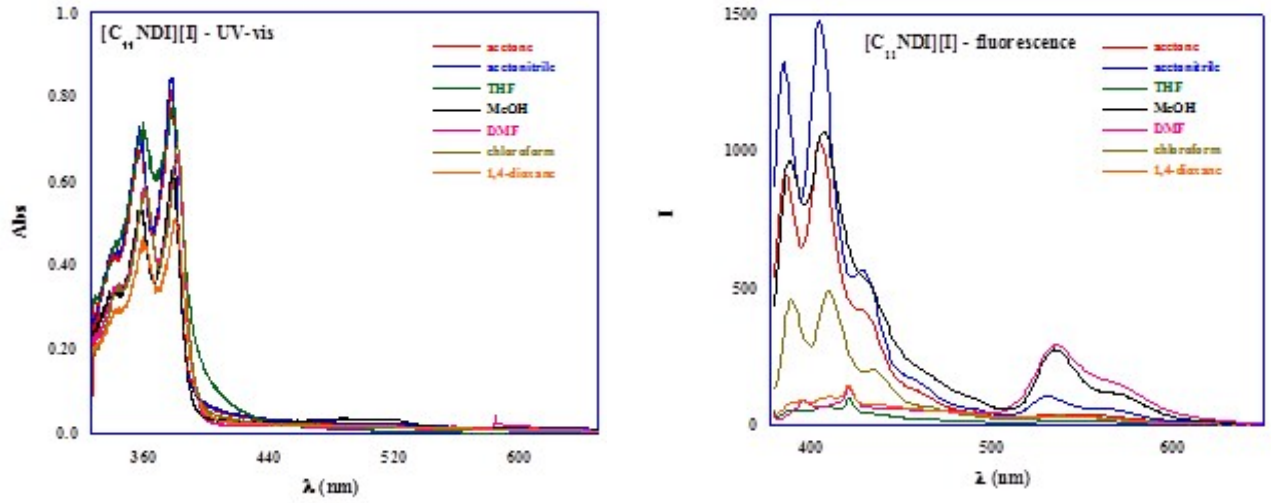
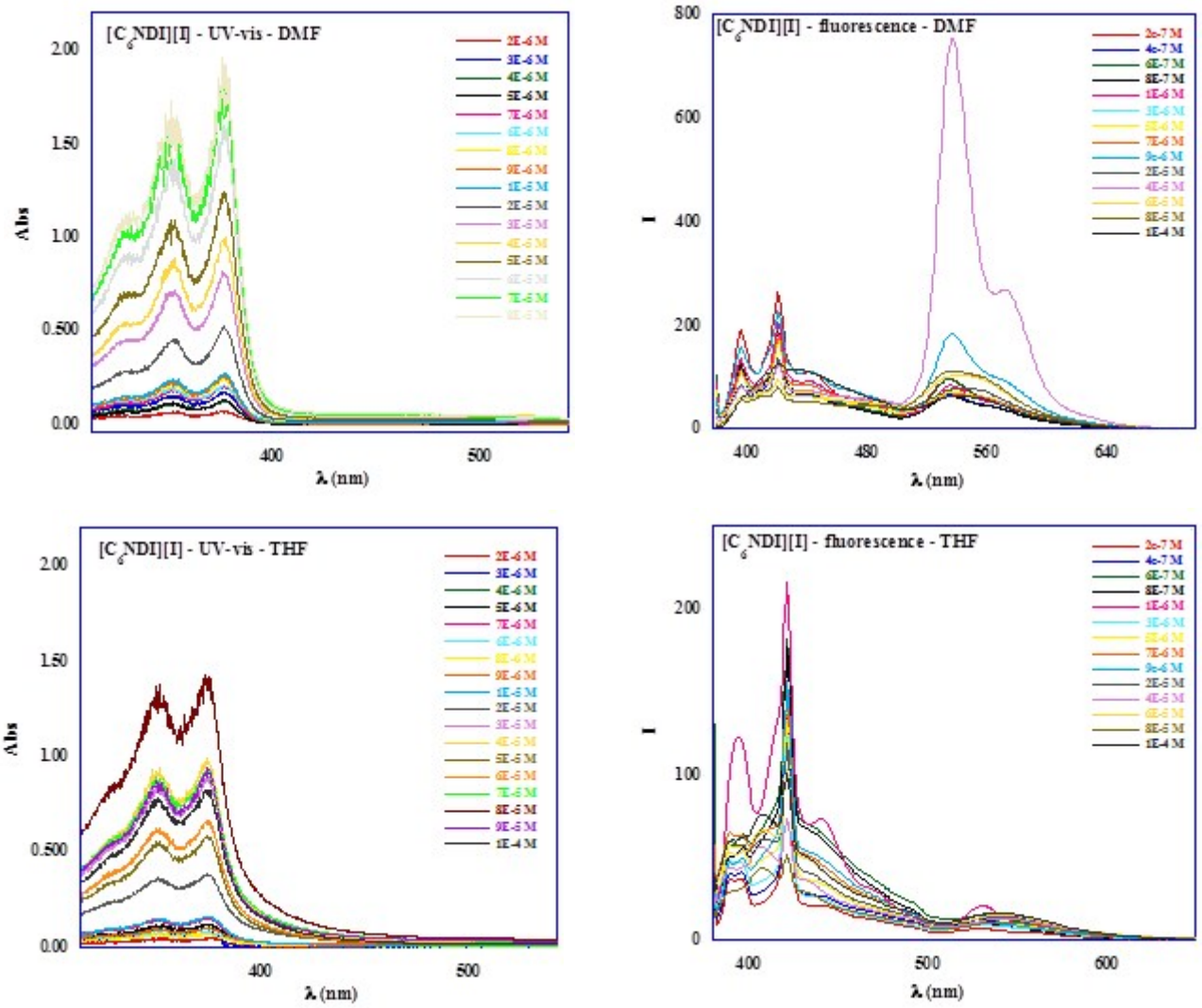
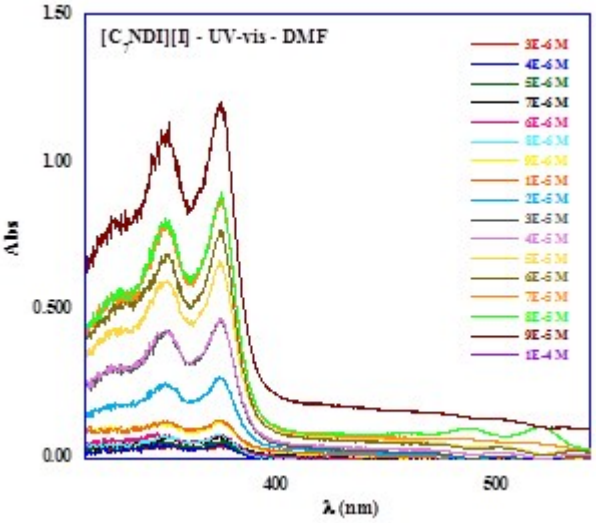
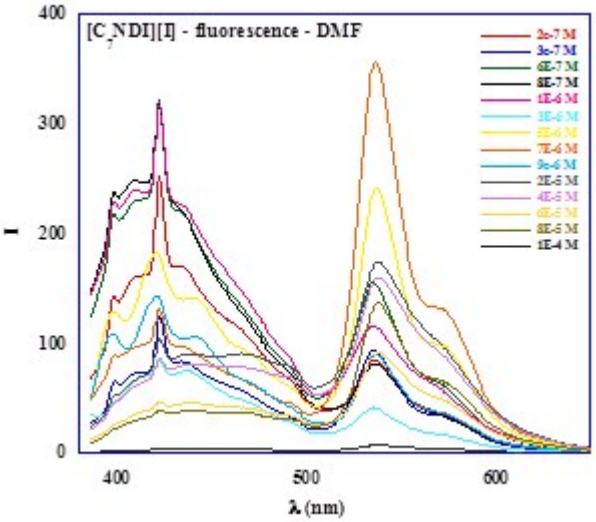
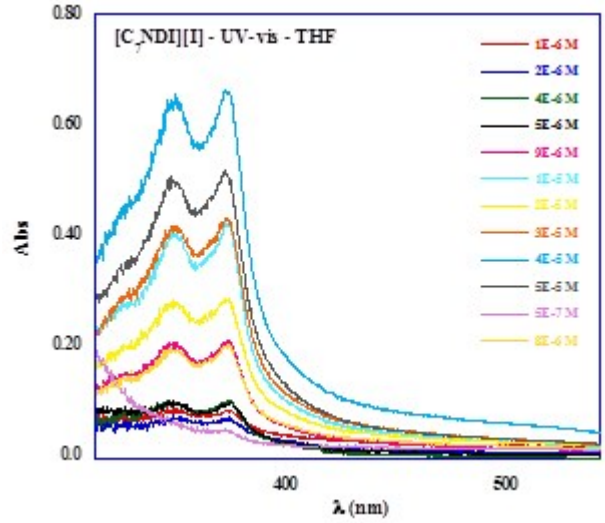


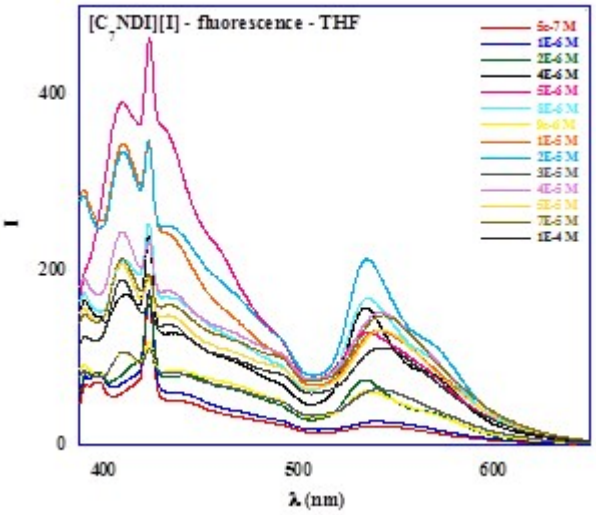
Figure S2. UV-vis and fluorescence spectra of salts as function of solvent. Fluorescence intensities are in arbitrary units.

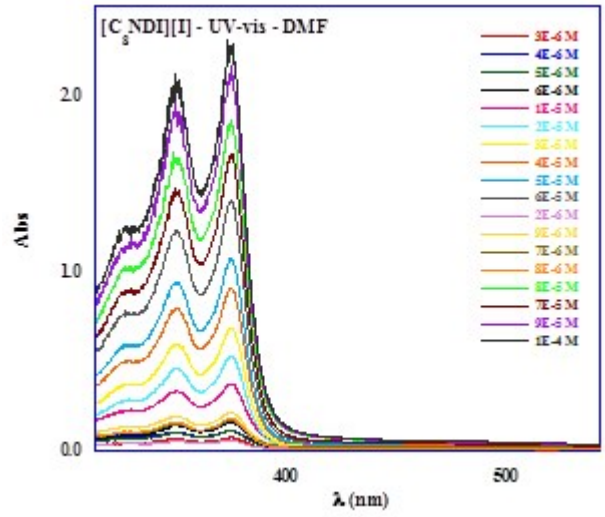


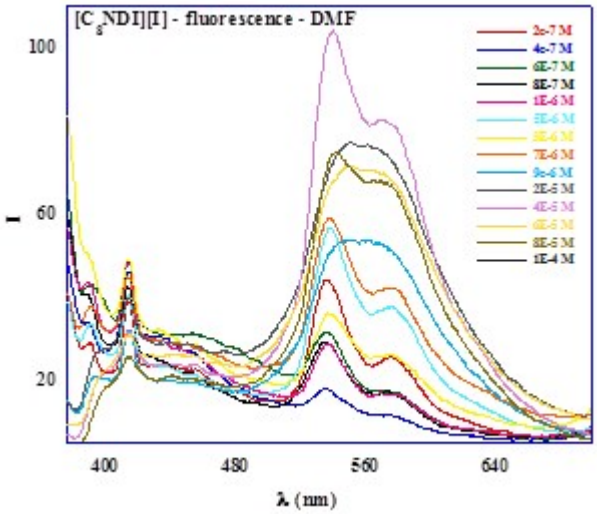

[C7NDI][I] - UV-vis - DMF
Abs
λ (nm)
3E-6 M
4E-6 M
5E-6 M
7E-6 M
6E-6 M
8E-6 M
9E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
6E-5 M
7E-5 M
8E-5 M
9E-5 M
1E-4 M

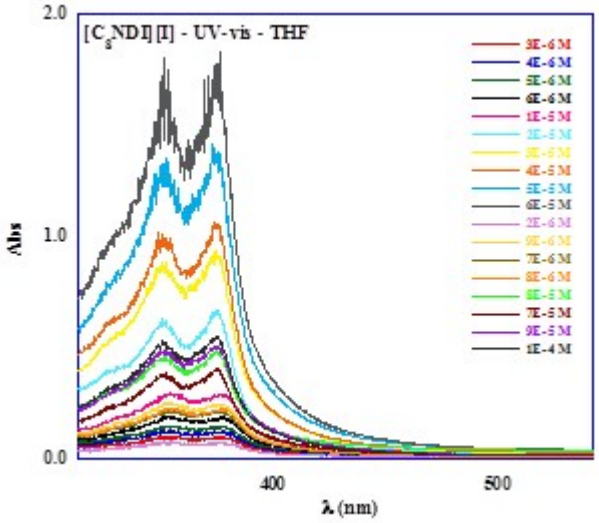

[C7NDI][I] - fluorescence - DMF
I
λ (nm)
2e-7 M
3e-7 M
6E-7 M
8E-7 M
1E-6 M
3E-6 M
5E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
6E-5 M
8E-5 M
1E-4 M

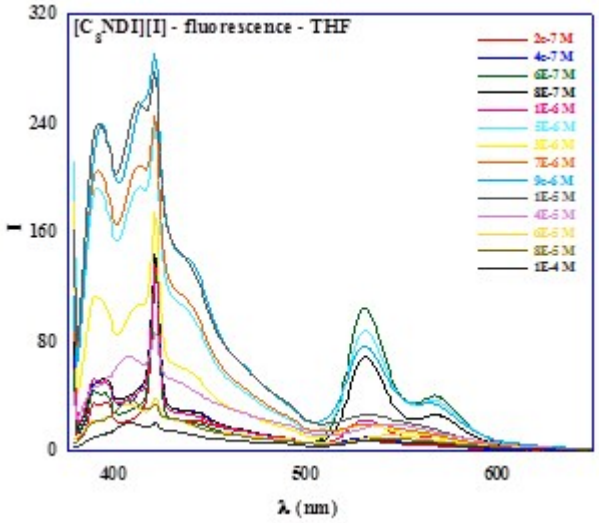

[C7NDI][I] - UV-vis - THF
Abs
λ (nm)
1E-6 M
2E-6 M
4E-6 M
5E-6 M
9E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
5E-7 M
8E-6 M

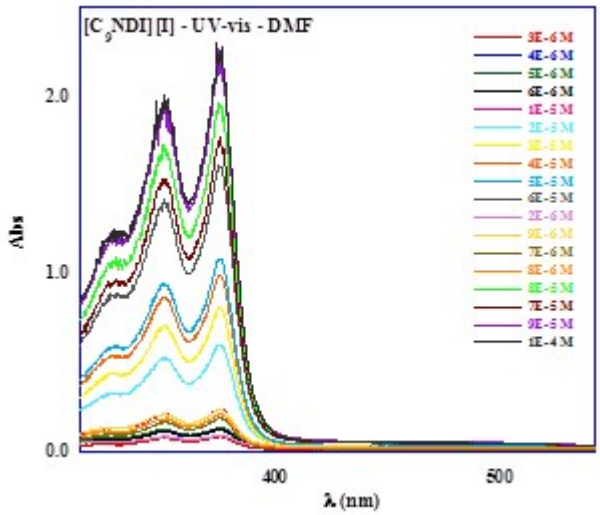

[C7NDI][I] - fluorescence - THF
I
λ (nm)
5e-7 M
1E-6 M
2E-6 M
4E-6 M
5E-6 M
8E-6 M
9e-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
7E-5 M
1E-4 M

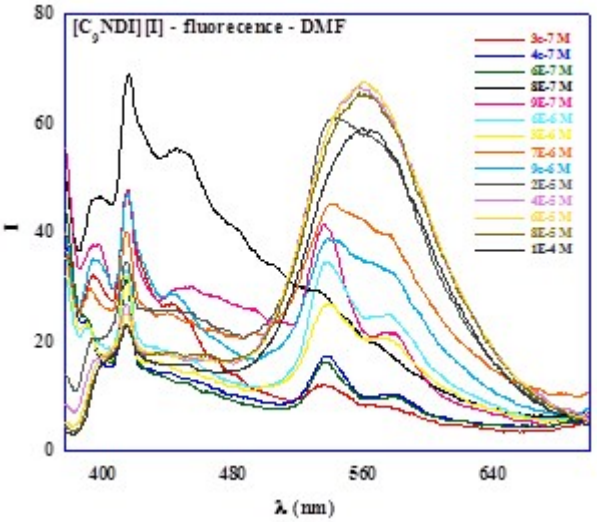

[C8NDI][I] - UV-vis - DMF
Abs
λ (nm)
3E-6 M
4E-6 M
5E-6 M
6E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
6E-5 M
2E-5 M
9E-6 M
7E-6 M
8E-6 M
8E-6 M
7E-5 M
9E-5 M
1E-4 M

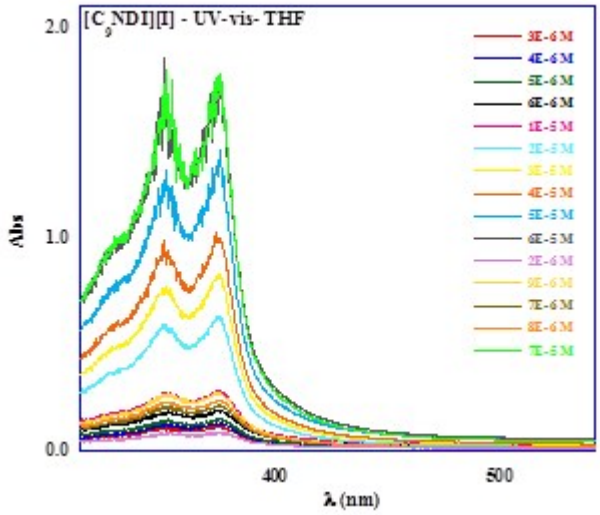

[C8NDI][I] - fluorescence - DMF
I
λ (nm)
2e-7 M
4e-7 M
6E-7 M
8E-7 M
1E-6 M
5E-6 M
8E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
6E-5 M
8E-5 M
1E-4 M

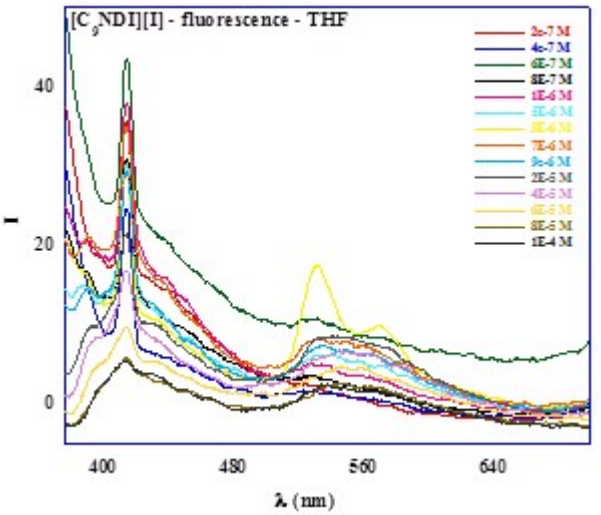

[C8NDI][I] - UV-vis - THF
3E-6 M
4E-6 M
5E-6 M
6E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
6E-5 M
2E-6 M
9E-6 M
7E-6 M
8E-6 M
9E-5 M
7E-5 M
9E-5 M
1E-4 M
Abs
λ (nm)

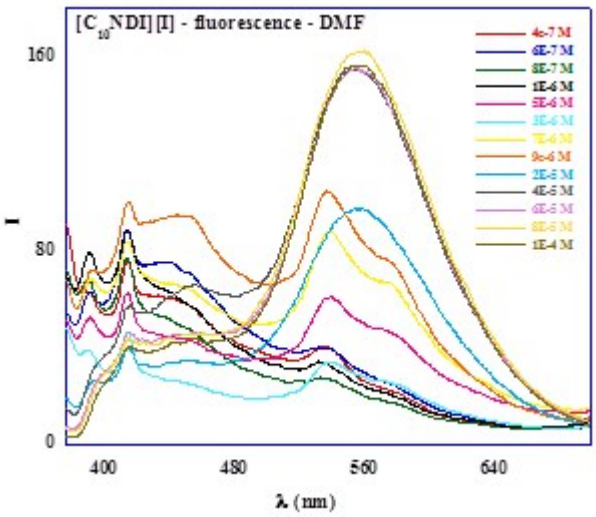

[C8NDI][I] - fluorescence - THF
2e-7 M
4e-7 M
6E-7 M
8E-7 M
1E-6 M
5E-6 M
3E-6 M
7E-6 M
9e-6 M
1E-5 M
4E-5 M
6E-5 M
8E-5 M
1E-4 M
I
λ (nm)

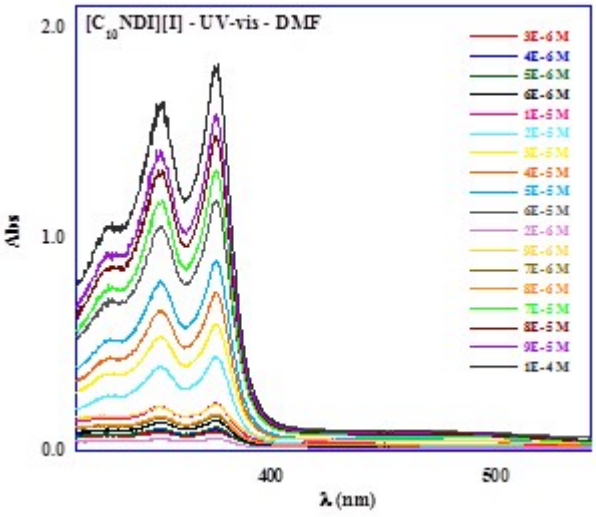

[C9NDI][I] - UV-vis - DMF
3E-6 M
4E-6 M
5E-6 M
6E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
6E-5 M
2E-6 M
9E-6 M
7E-6 M
8E-6 M
8E-5 M
7E-5 M
9E-5 M
1E-4 M
Abs
λ (nm)

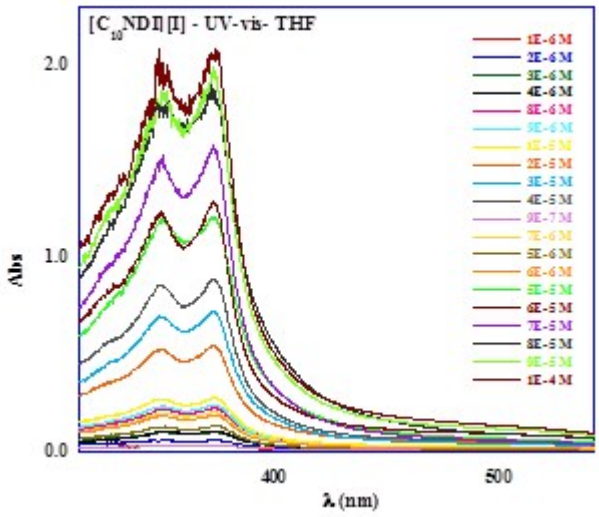

[C9NDI][I] - fluorescence - DMF
3e-7 M
4e-7 M
6E-7 M
8E-7 M
9E-7 M
6E-6 M
3E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
6E-5 M
8E-5 M
1E-4 M
I
λ (nm)

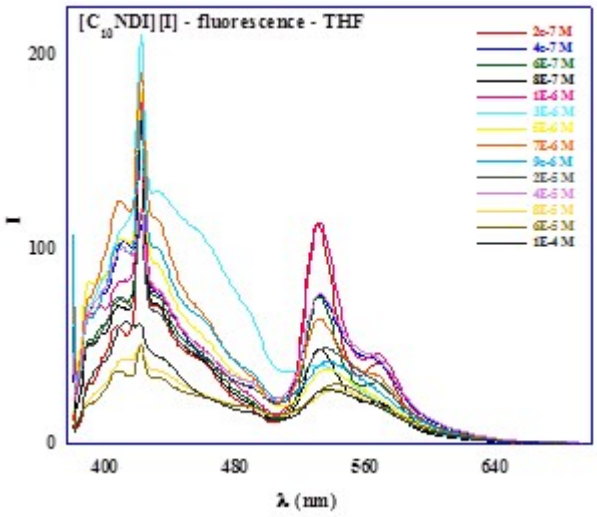

[C9NDI][I] - UV-vis- THF
3E-6 M
4E-6 M
5E-6 M
6E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
6E-5 M
2E-6 M
9E-6 M
7E-6 M
8E-6 M
7E-5 M
Abs
λ (nm)

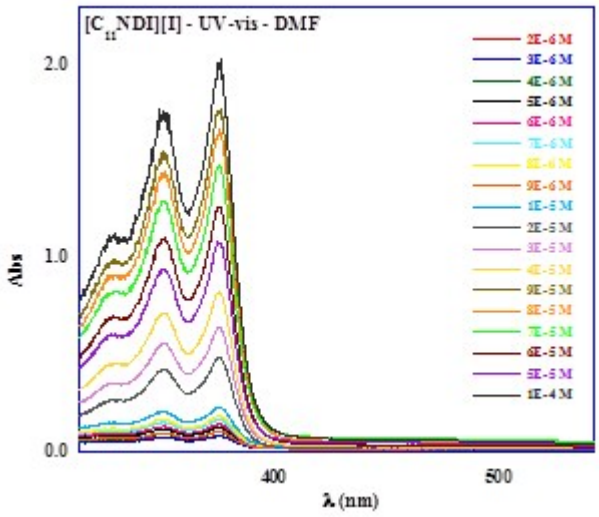

[C9NDI][I] - fluorescence - THF
2e-7 M
4e-7 M
6E-7 M
8E-7 M
1E-6 M
5E-6 M
3E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
6E-5 M
8E-5 M
1E-4 M
I
λ (nm)

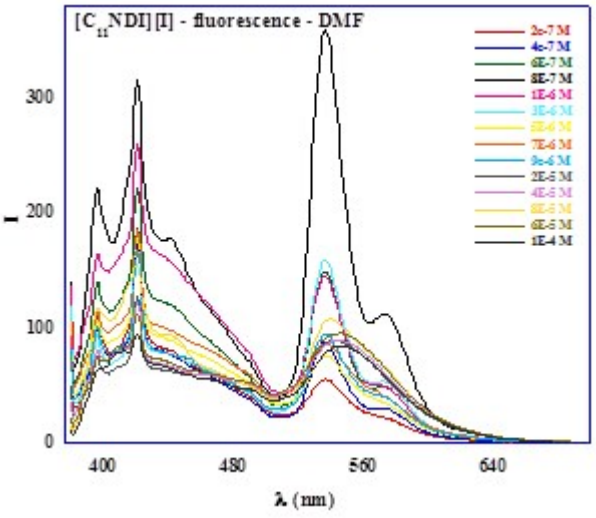

[C10NDI][I] - fluorescence - DMF
I
λ (nm)
4e-7 M
6E-7 M
8E-7 M
1E-6 M
5E-6 M
3E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
6E-5 M
8E-5 M
1E-4 M

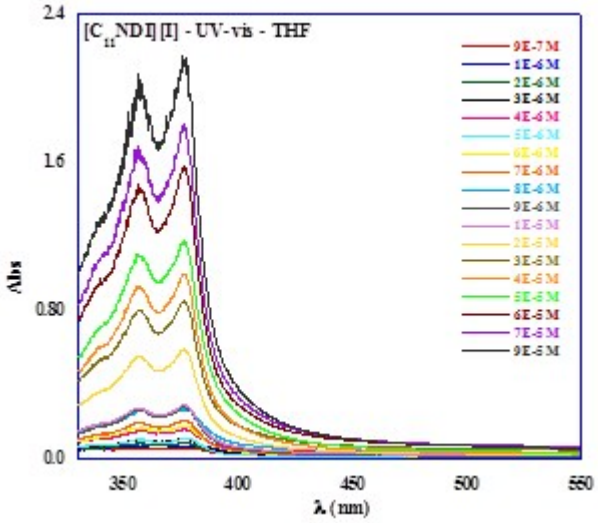

[C10NDI][I] - UV-vis - DMF
Abs
λ (nm)
3E-6 M
4E-6 M
5E-6 M
6E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
5E-5 M
6E-5 M
2E-6 M
9E-6 M
7E-6 M
8E-6 M
7E-5 M
8E-5 M
9E-5 M
1E-4 M

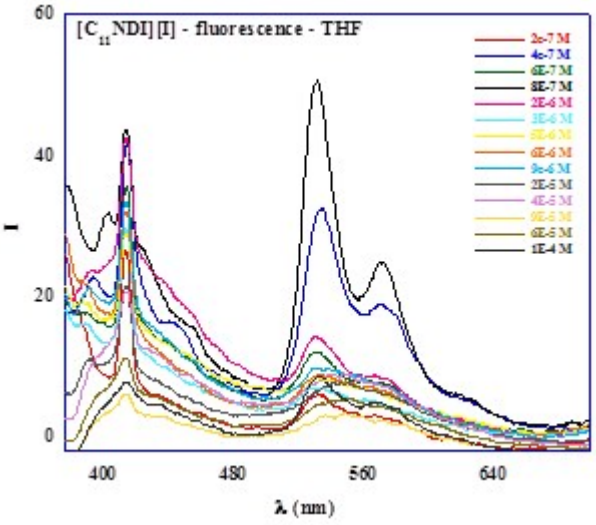

[C10NDI][I] - UV-vis- THF
Abs
λ (nm)
1E-6 M
2E-6 M
3E-6 M
4E-6 M
5E-6 M
9E-6 M
6E-5 M
2E-5 M
3E-5 M
4E-5 M
9E-7 M
7E-6 M
5E-6 M
6E-6 M
8E-5 M
6E-5 M
7E-5 M
8E-5 M
9E-5 M
1E-4 M

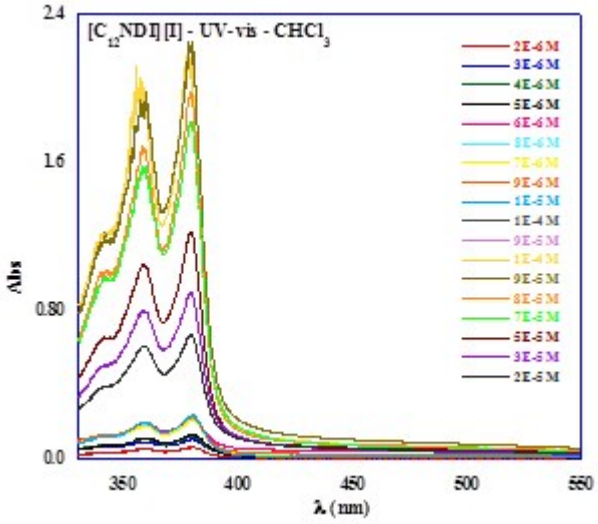

[C10NDI][I] - fluorescence - THF
I
λ (nm)
2e-7 M
4e-7 M
6E-7 M
8E-7 M
1E-6 M
3E-6 M
5E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
8E-5 M
6E-5 M
1E-4 M

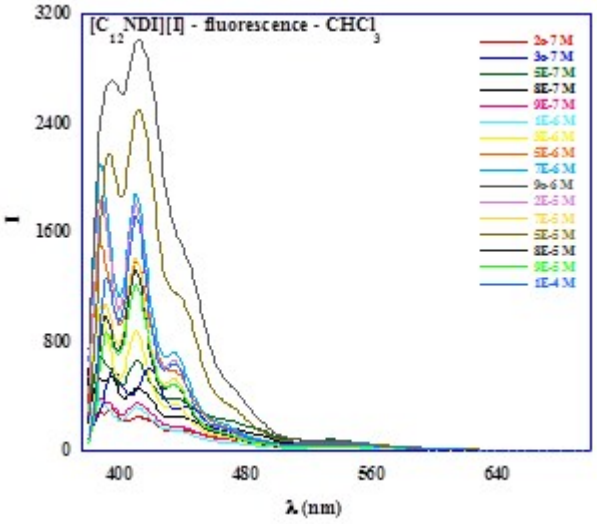

[C11NDI][I] - UV-vis - DMF
Abs
λ (nm)
2E-6 M
3E-6 M
4E-6 M
5E-6 M
6E-6 M
7E-6 M
8E-6 M
9E-6 M
1E-5 M
2E-5 M
3E-5 M
4E-5 M
9E-5 M
8E-5 M
7E-5 M
6E-5 M
5E-5 M
1E-4 M

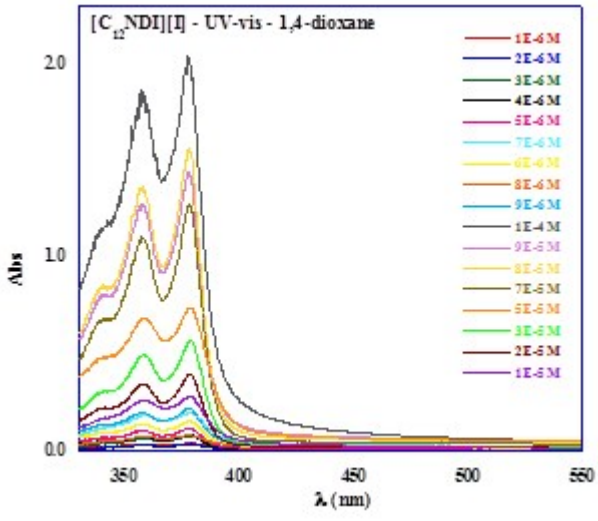

[C11NDI][I] - fluorescence - DMF
I
λ (nm)
2e-7 M
4e-7 M
6E-7 M
8E-7 M
1E-6 M
3E-6 M
5E-6 M
7E-6 M
9e-6 M
2E-5 M
4E-5 M
8E-5 M
6E-5 M
1E-4 M

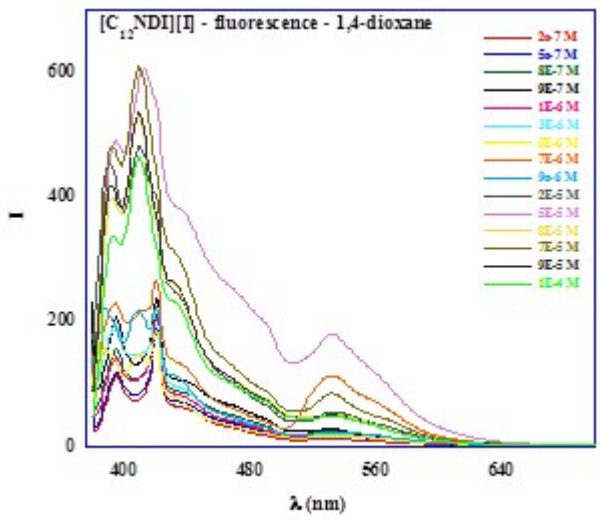

[C11NDI][I] - UV-vis - THF
Abs
λ (nm)


[C11NDI][I] - fluorescence - THF
I
λ (nm)


[C12NDI][I] - UV-vis - CHCl3
Abs
λ (nm)


[C12NDI][I] - fluorescence - CHCl3
I
λ (nm)


[C12NDI][I] - UV-vis - 1,4-dioxane
Abs
λ (nm)


[C12NDI][I] - fluorescence - 1,4-dioxane
I
λ (nm)

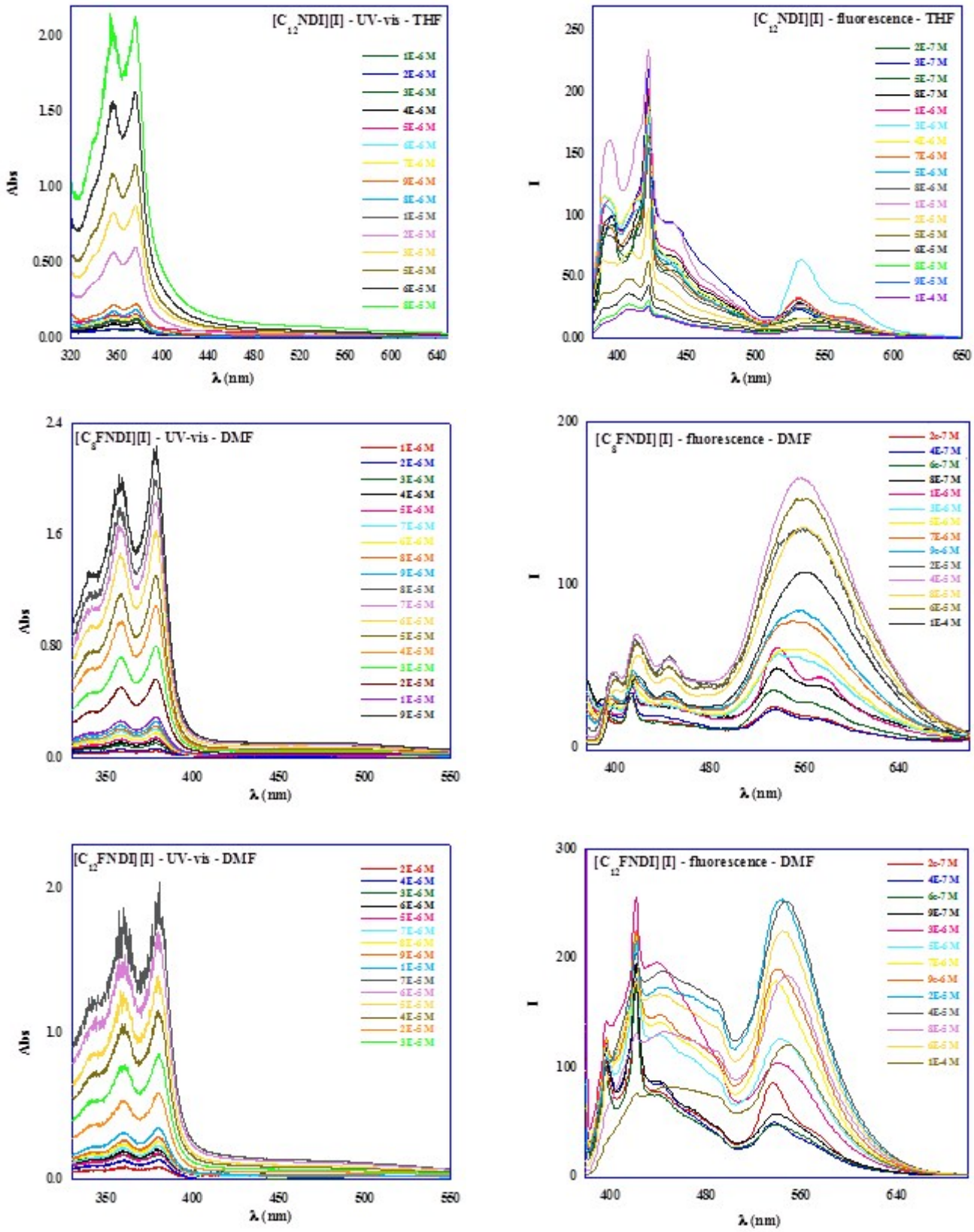
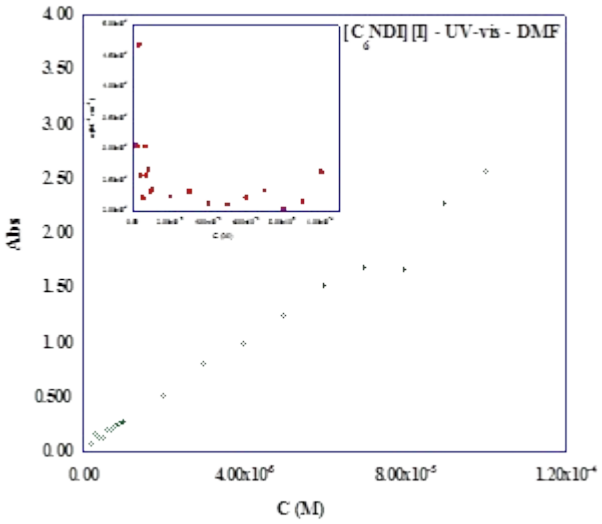
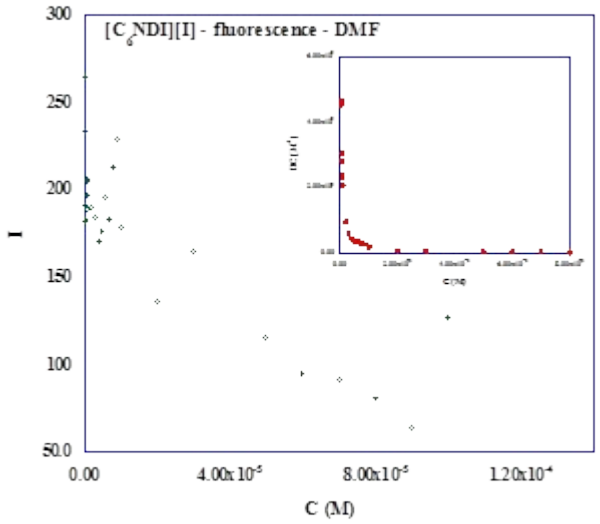
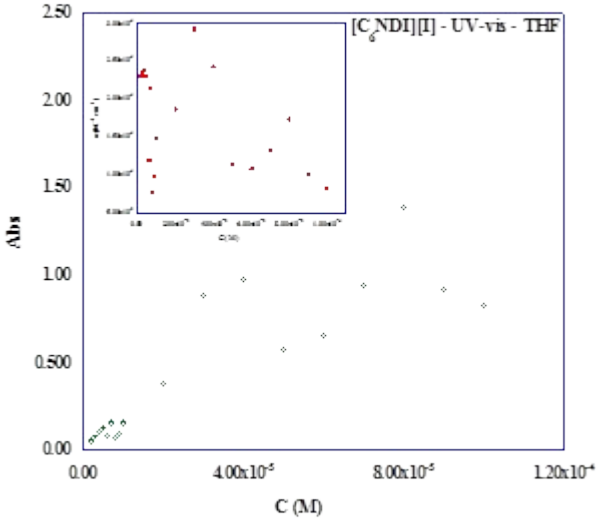
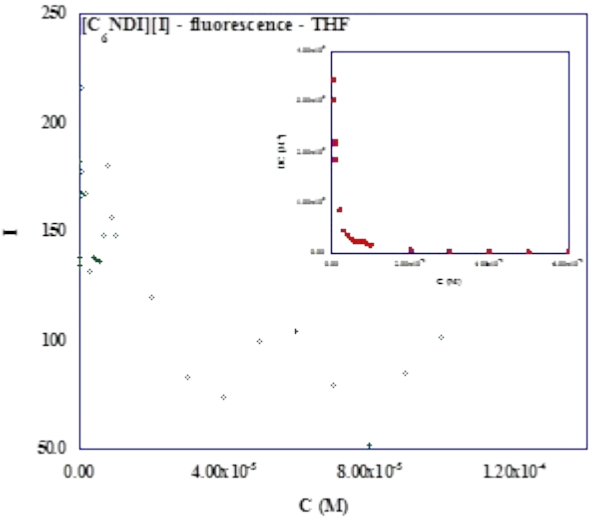


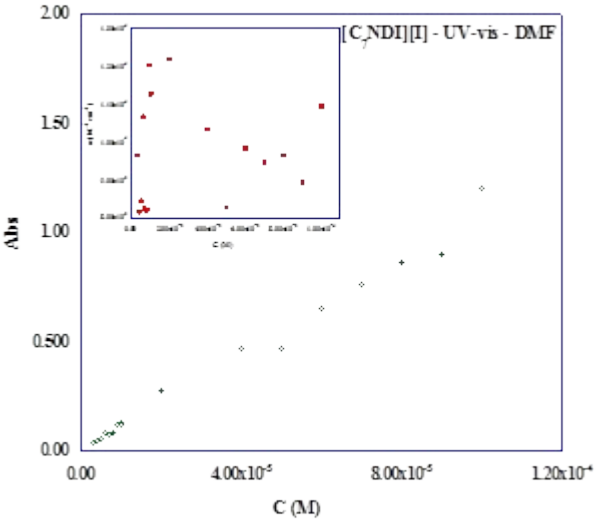
Figure S3. UV-vis and fluorescence (λ_{ex} = 362 nm) of salts as a function of concentration and solvent. Fluorescence intensities are in arbitrary units.

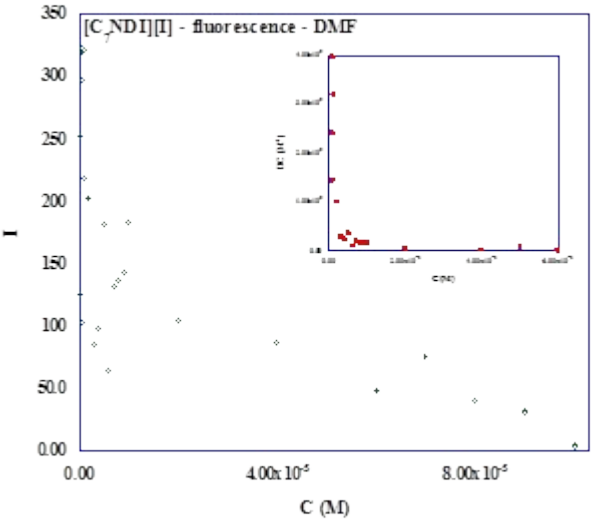

[C6NDI][I] - UV-vis - DMF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
1.20x10-4
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.500
0.00

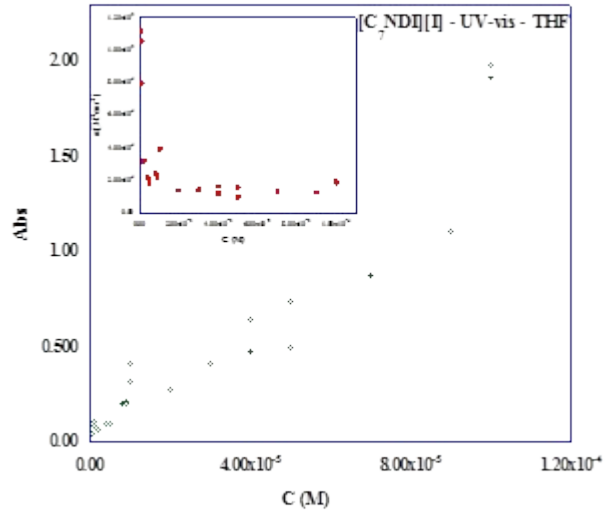

[C6NDI][I] - fluorescence - DMF
I
C (M)
0.00
4.00x10-5
8.00x10-5
1.20x10-4
300
250
200
150
100
50.0

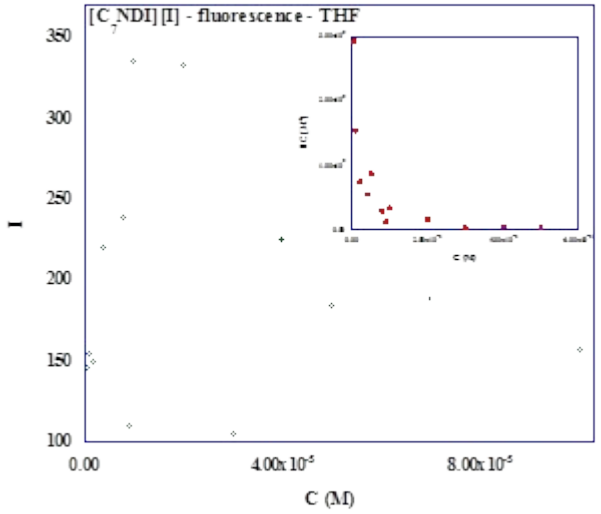

[C6NDI][I] - UV-vis - THF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
1.20x10-4
2.50
2.00
1.50
1.00
0.500
0.00

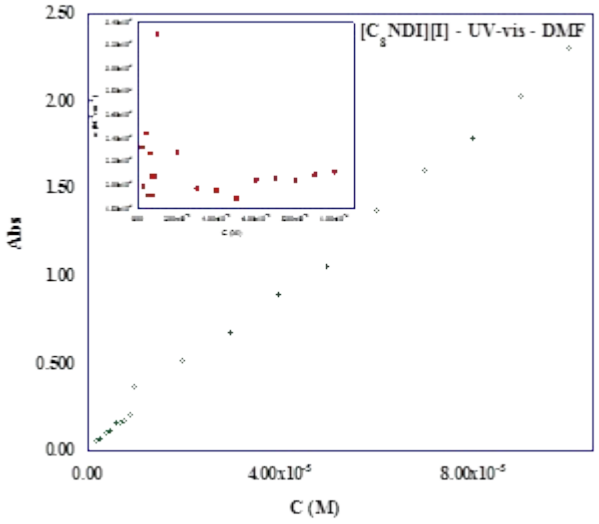

[C6NDI][I] - fluorescence - THF
I
C (M)
0.00
4.00x10-5
8.00x10-5
1.20x10-4
250
200
150
100
50.0

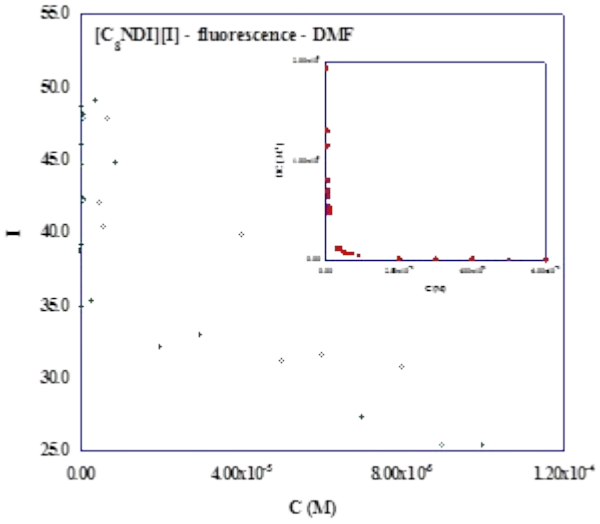

[C7NDI][I] - UV-vis - DMF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
1.20x10-4
2.00
1.50
1.00
0.500
0.00

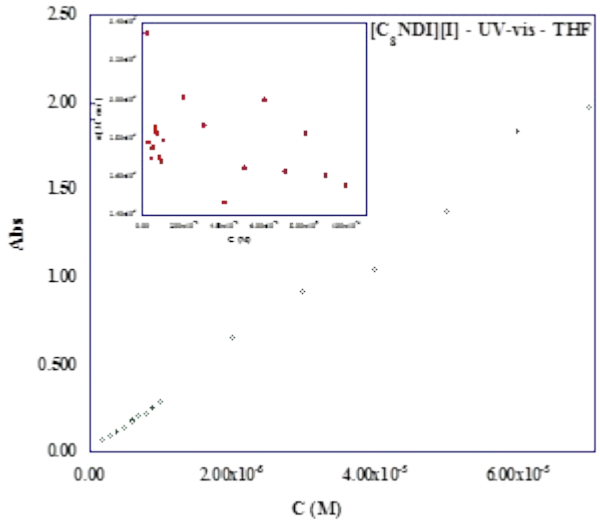

[C7NDI][I] - fluorescence - DMF
I
C (M)
0.00
4.00x10-5
8.00x10-5
350
300
250
200
150
100
50.0
0.00

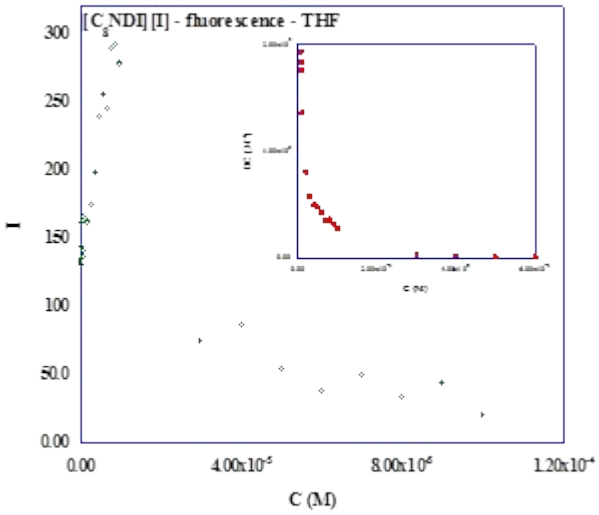

[C7NDI][I] - UV-vis - THF
Abs
C (M)
0.00
0.500
1.00
1.50
2.00
4.00x10-5
8.00x10-5
1.20x10-4

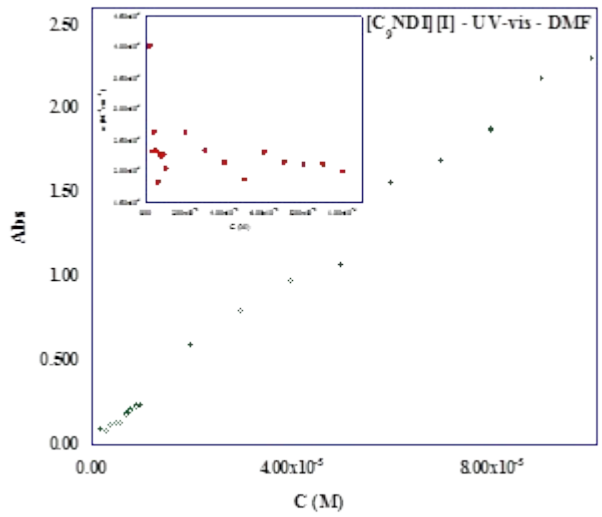

[C7NDI][I] - fluorescence - THF
I
C (M)
100
150
200
250
300
350
0.00
4.00x10-5
8.00x10-5

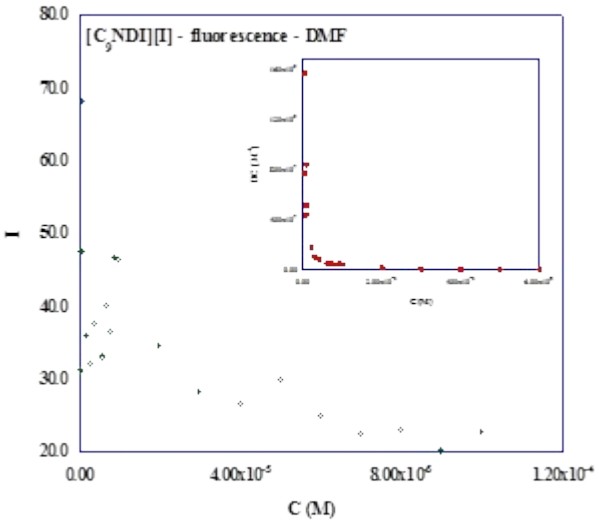

[C8NDI][I] - UV-vis - DMF
Abs
C (M)
0.00
0.500
1.00
1.50
2.00
2.50
0.00
4.00x10-5
8.00x10-5

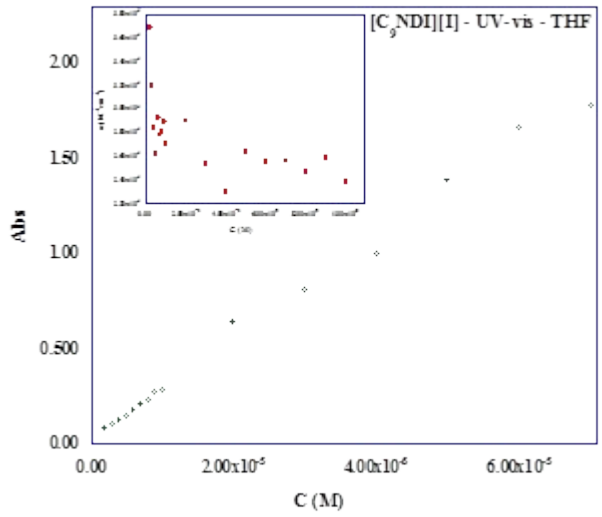

[C8NDI][I] - fluorescence - DMF
I
C (M)
25.0
30.0
35.0
40.0
45.0
50.0
55.0
0.00
4.00x10-5
8.00x10-6
1.20x10-4

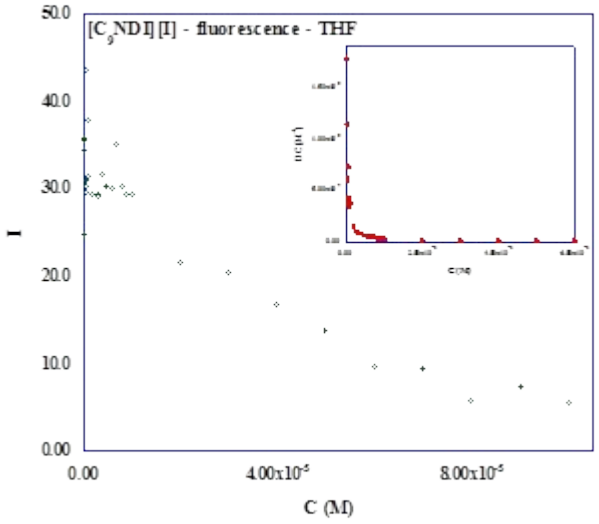

[C8NDI][I] - UV-vis - THF
Abs
C (M)
0.00
0.500
1.00
1.50
2.00
2.50
0.00
2.00x10-6
4.00x10-5
6.00x10-5

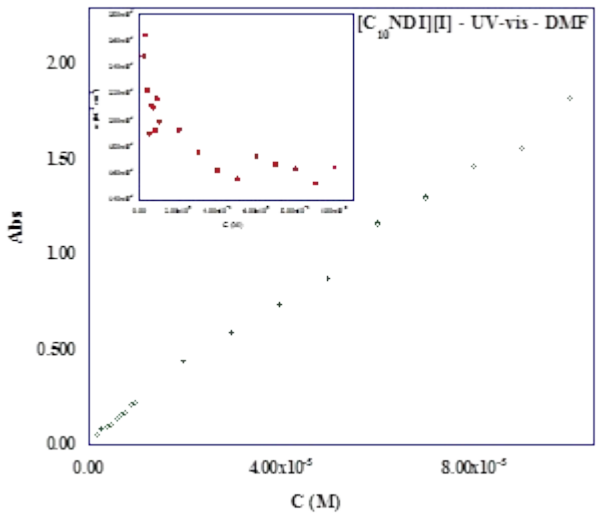

[C8NDI][I] - fluorescence - THF
I
C (M)
0.00
50.0
100
150
200
250
300
0.00
4.00x10-5
8.00x10-6
1.20x10-4

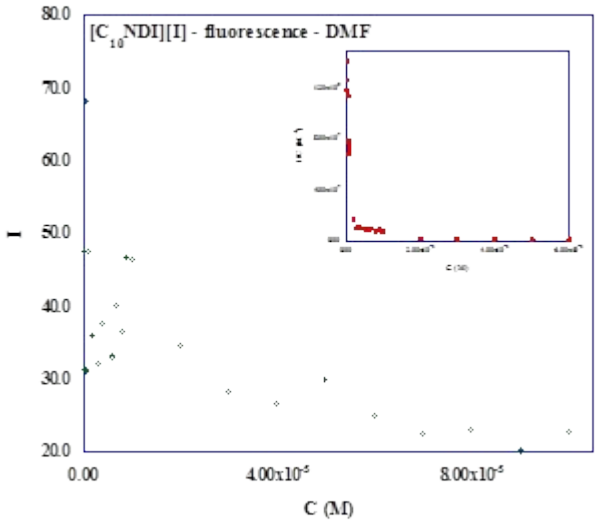

[C9NDI][I] - UV-vis - DMF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
0.500
1.00
1.50
2.00
2.50

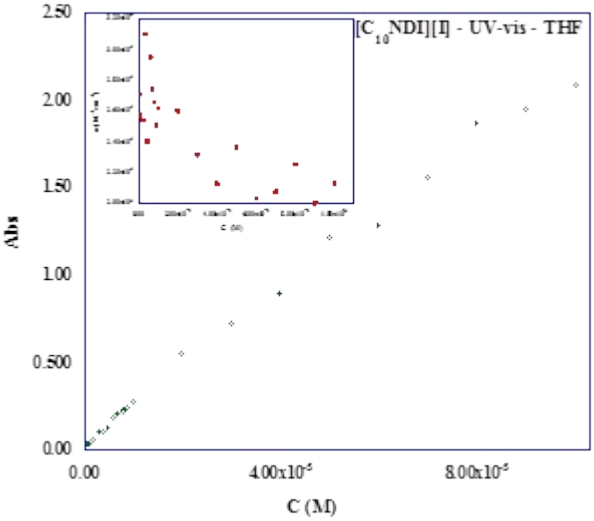

[C9NDI][I] - fluorescence - DMF
I
C (M)
0.00
4.00x10-5
8.00x10-5
1.20x10-4
20.0
30.0
40.0
50.0
60.0
70.0
80.0

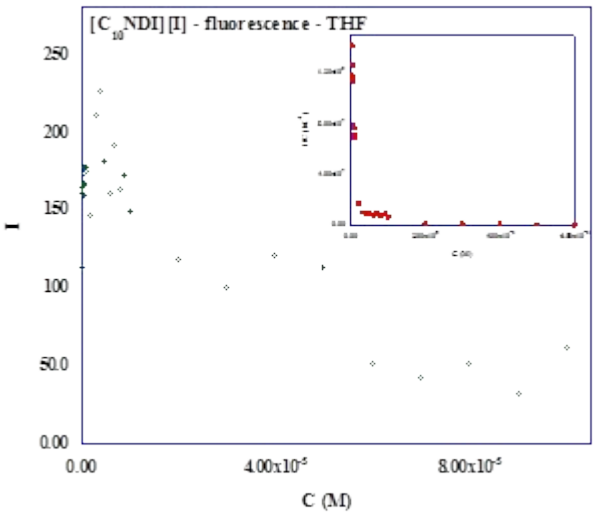

[C9NDI][I] - UV-vis - THF
Abs
C (M)
0.00
2.00x10-5
4.00x10-5
6.00x10-5
0.500
1.00
1.50
2.00

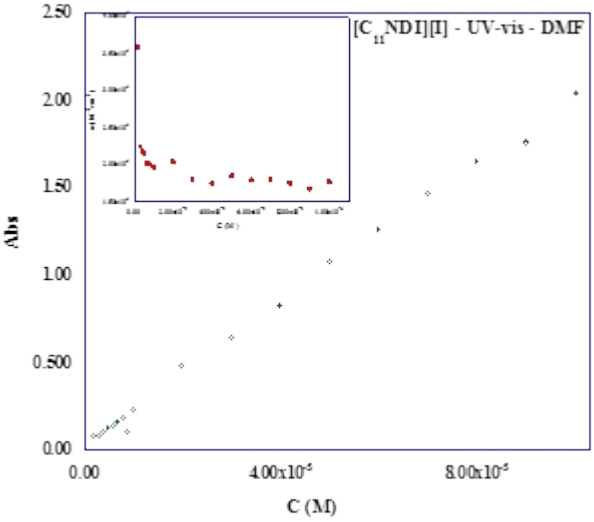

[C9NDI][I] - fluorescence - THF
I
C (M)
0.00
4.00x10-5
8.00x10-5
10.0
20.0
30.0
40.0
50.0

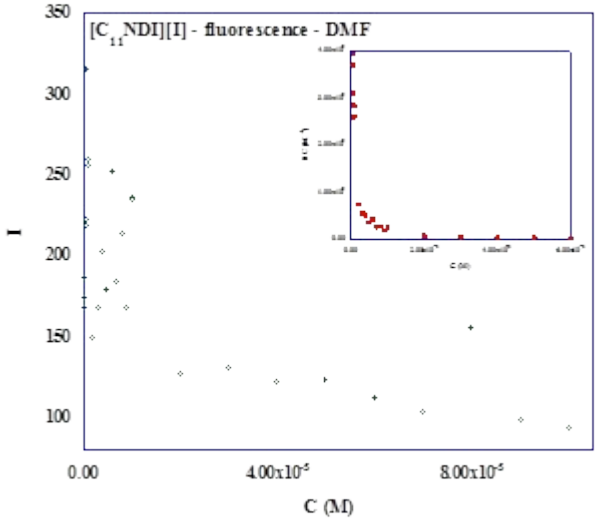

[C10NDI][I] - UV-vis - DMF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
0.500
1.00
1.50
2.00

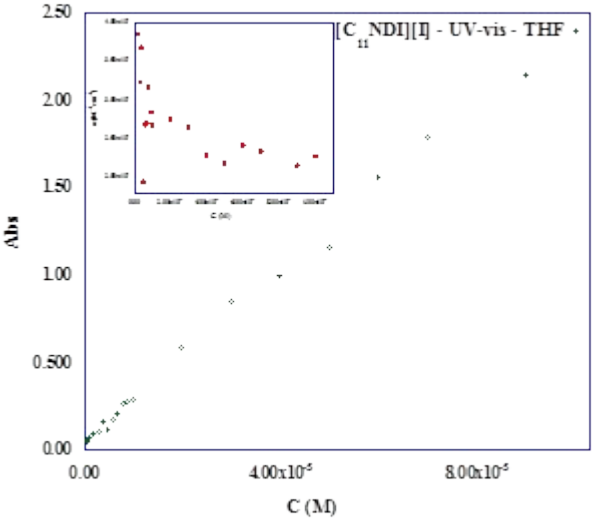

[C10NDI][I] - fluorescence - DMF
I
C (M)
0.00
4.00x10-5
8.00x10-5
20.0
30.0
40.0
50.0
60.0
70.0
80.0

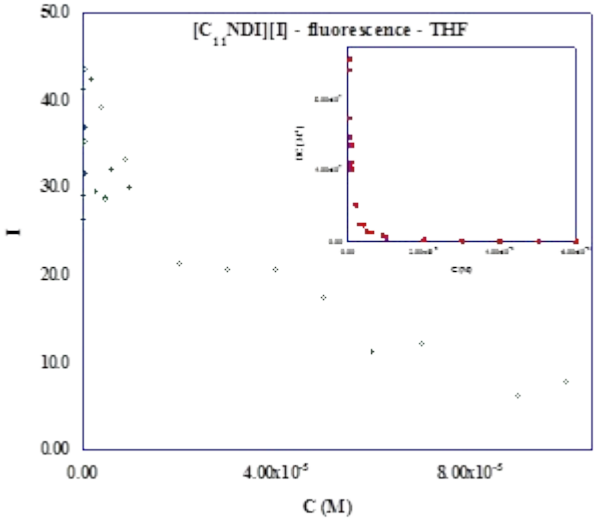

[C10NDI][I] - UV-vis - THF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
0.500
1.00
1.50
2.00
2.50

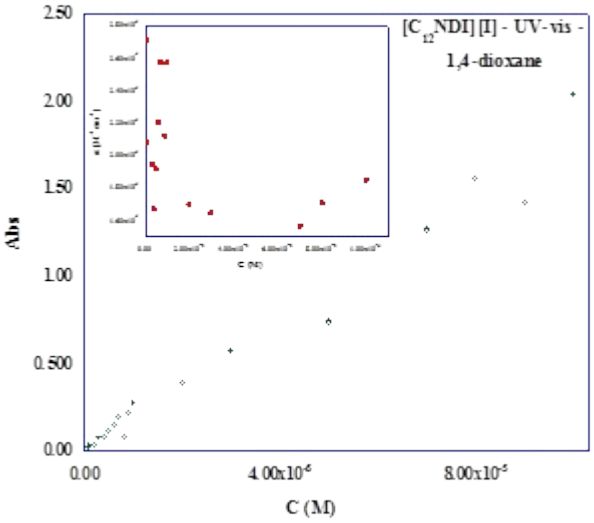

[C10NDI][I] - fluorescence - THF
I
C (M)
0.00
4.00x10-5
8.00x10-5
50.0
100
150
200
250

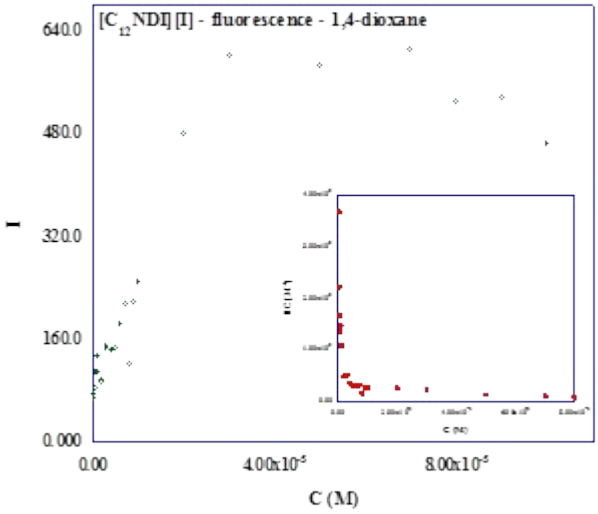

[C11NDI][I] - UV-vis - DMF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
0.500
1.00
1.50
2.00
2.50

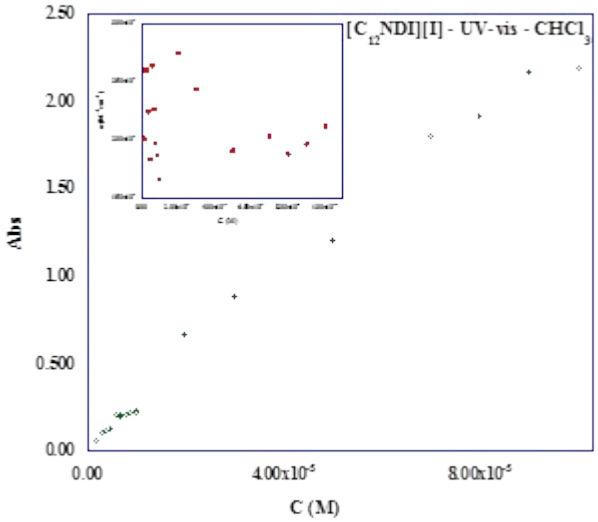

[C11NDI][I] - fluorescence - DMF
I
C (M)
0.00
4.00x10-5
8.00x10-5
100
150
200
250
300
350

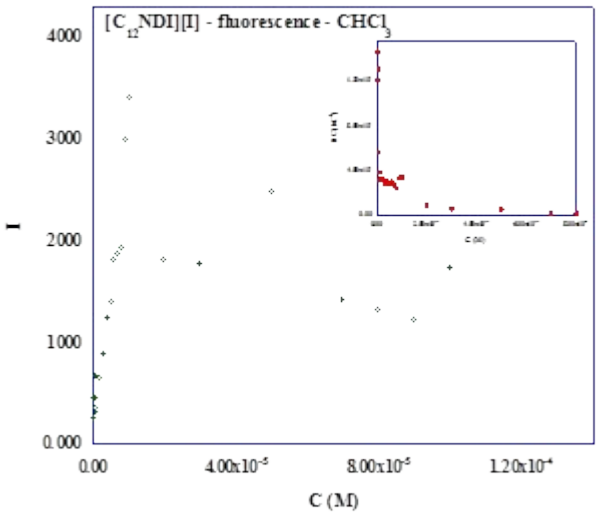

[C11NDI][I] - UV-vis - THF
Abs
C (M)
0.00
4.00x10-5
8.00x10-5
0.500
1.00
1.50
2.00
2.50

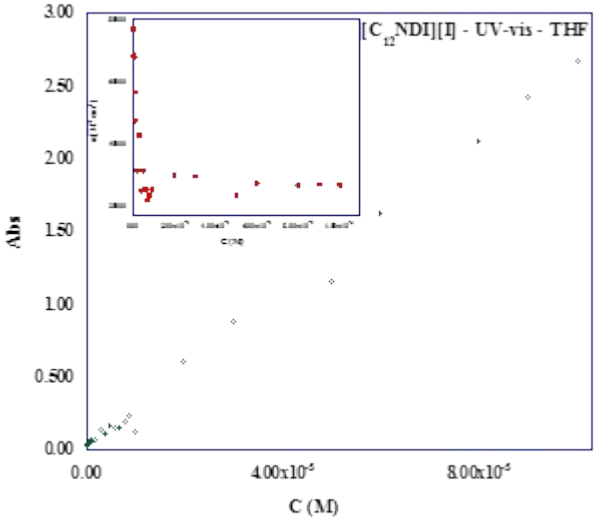

[C11NDI][I] - fluorescence - THF
I
C (M)
0.00
4.00x10-5
8.00x10-5
10.0
20.0
30.0
40.0
50.0

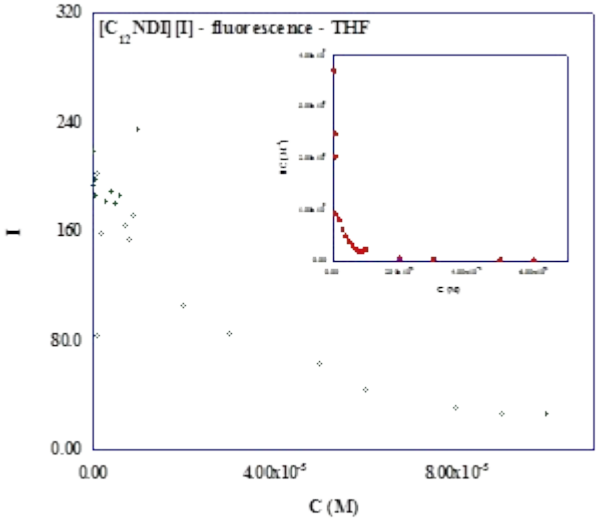

[C12NDI][I] - UV-vis - 1,4-dioxane
Abs
C (M)
0.00
0.500
1.00
1.50
2.00
2.50
4.00x10-5
8.00x10-5


[C12NDI][I] - fluorescence - 1,4-dioxane
I
C (M)
0.000
160.0
320.0
480.0
640.0
0.00
4.00x10-5
8.00x10-5


[C12NDI][I] - UV-vis - CHCl3
Abs
C (M)
0.00
0.500
1.00
1.50
2.00
2.50
4.00x10-5
8.00x10-5


[C12NDI][I] - fluorescence - CHCl3
I
C (M)
0.000
1000
2000
3000
4000
0.00
4.00x10-5
8.00x10-5
1.20x10-4


[C12NDI][I] - UV-vis - THF
Abs
C (M)
0.00
0.500
1.00
1.50
2.00
2.50
3.00
4.00x10-5
8.00x10-5


[C12NDI][I] - fluorescence - THF
I
C (M)
0.00
80.0
160
240
320
0.00
4.00x10-5
8.00x10-5

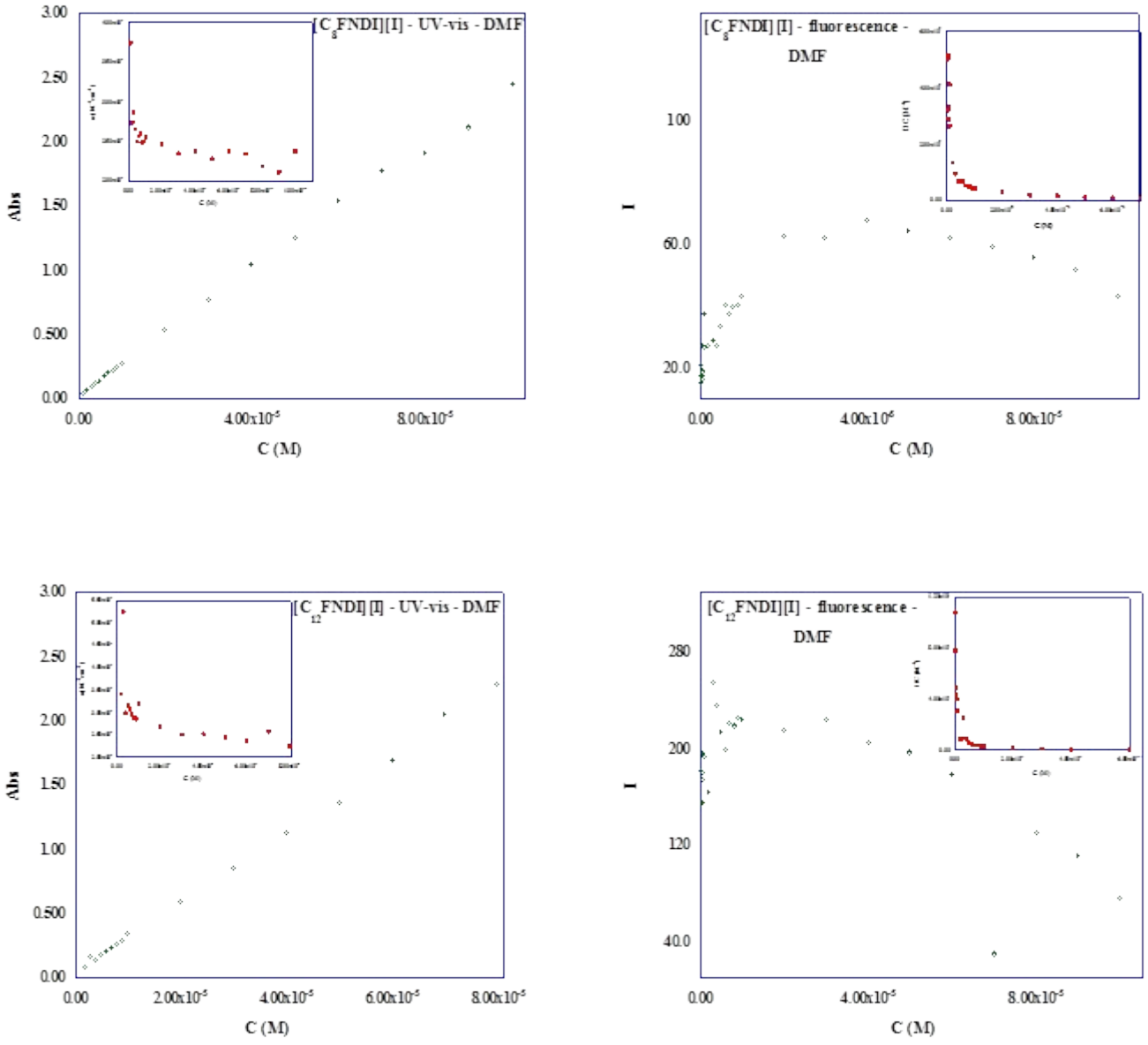
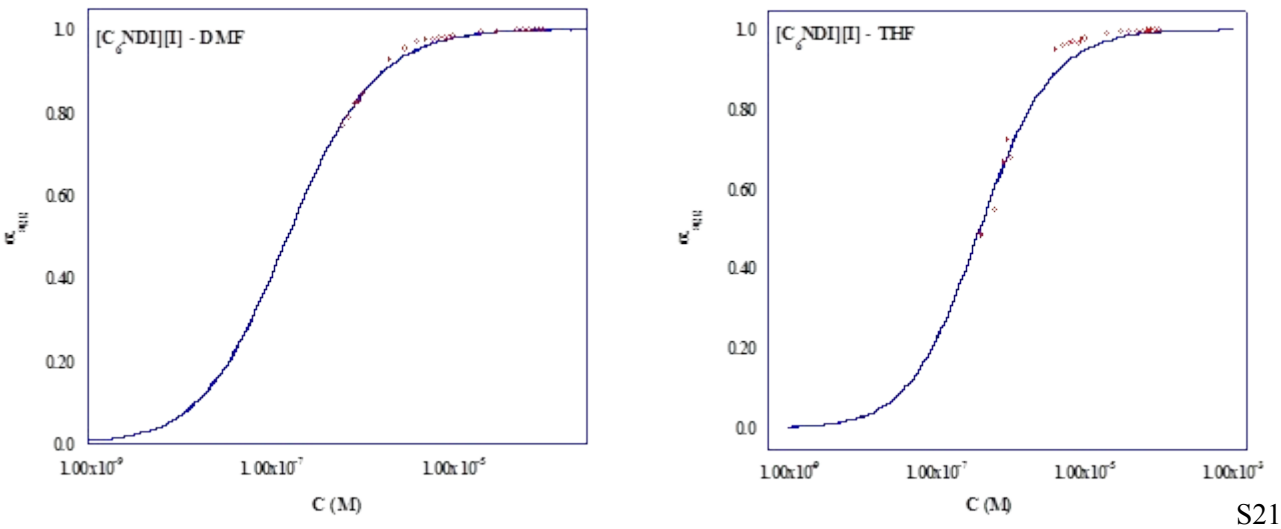
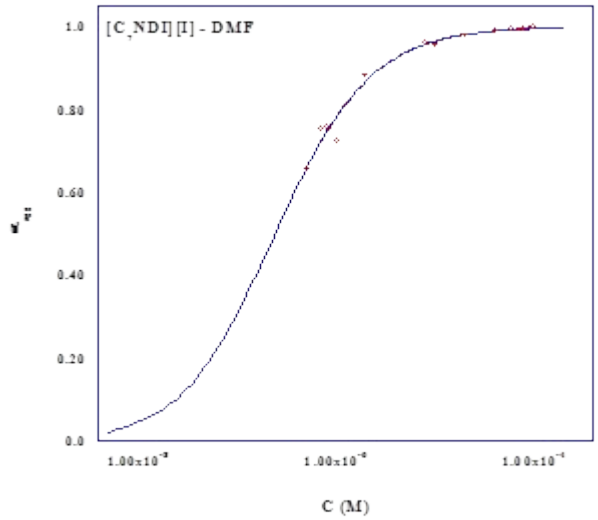
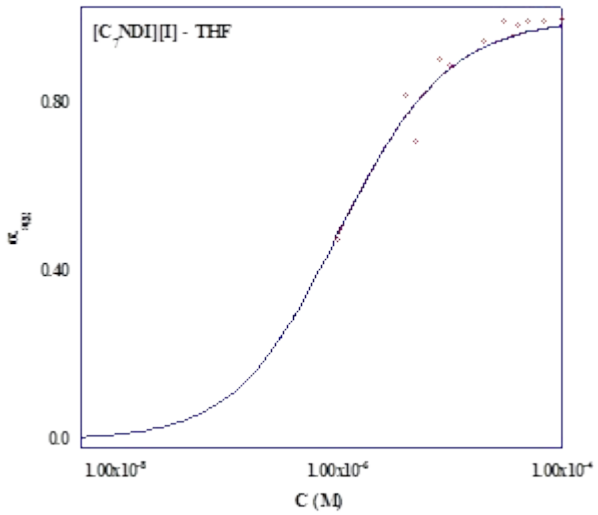
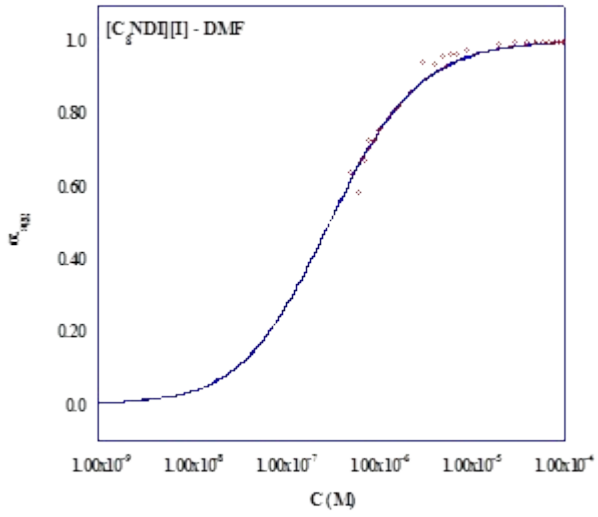


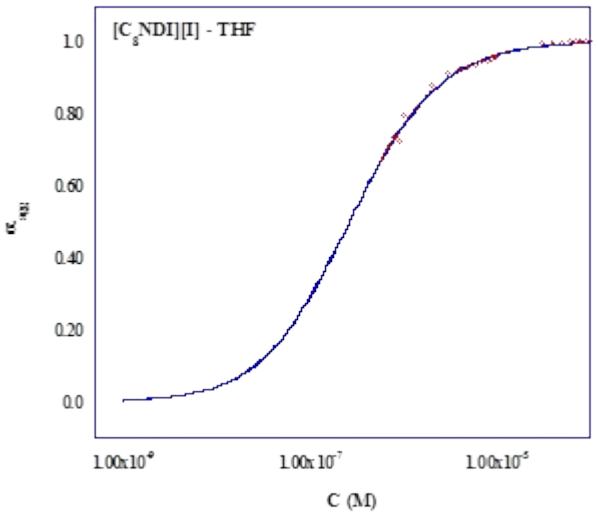
Figure S4. Absorbance and fluorescence intensity (arbitrary units) as a function of concentration and solvent. (Inset: trend of ε as a function of concentration; trend of I/C as function of concentration). I/C values were determined at 415 nm for **[C_8NDI][I]**in DMF, **[C_{10}NDI][I]** in THF and DMF. Moreover, I/C was determined at 533 nm for **[C_{12}NDI][I]** in dioxane, 435 nm **[C_{12}NDI][I]**in $CHCl_3$ and at 422 nm in all other cases.

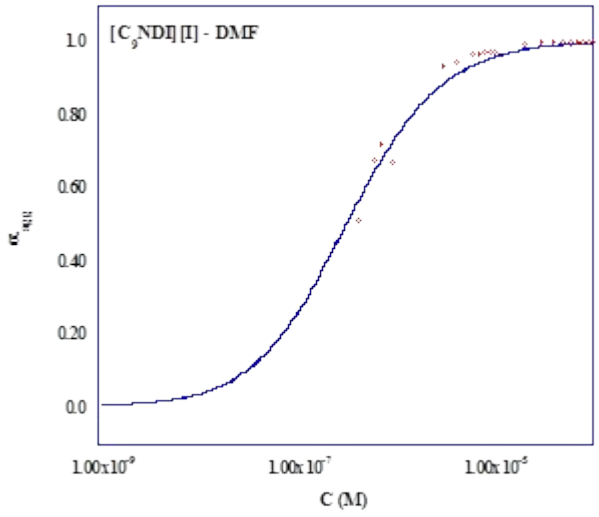


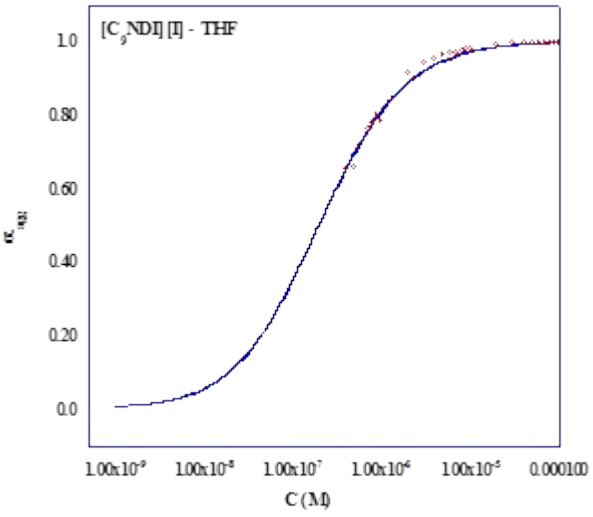

[C7NDI][I] - DMF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁶
1.00x10⁻⁴
C (M)

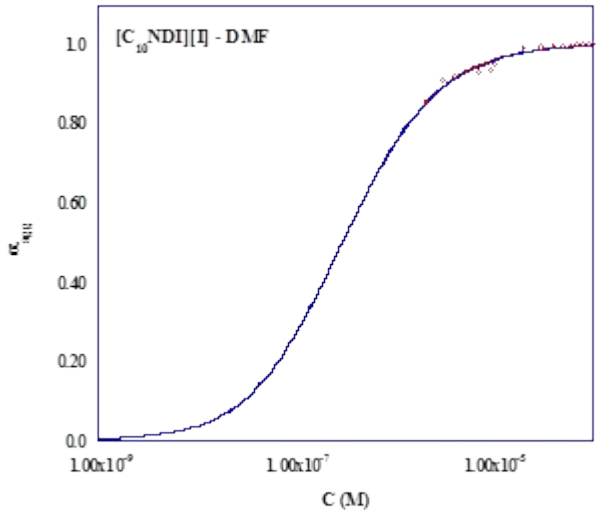

[C7NDI][I] - THF
0.80
0.40
0.0
1.00x10⁻⁸
1.00x10⁻⁶
1.00x10⁻⁴
C (M)

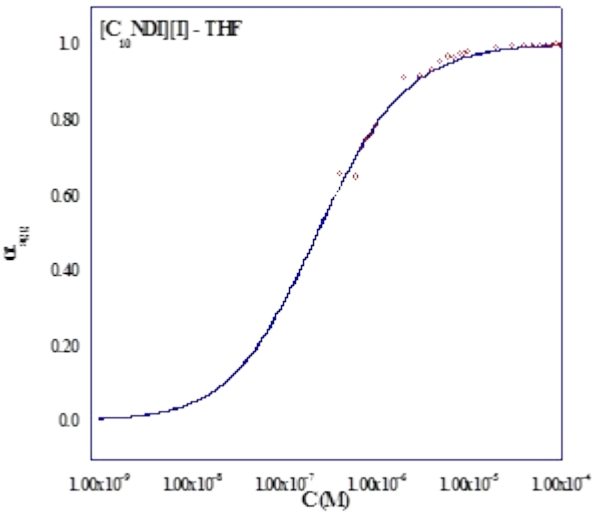

[C8NDI][I] - DMF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁸
1.00x10⁻⁷
1.00x10⁻⁶
1.00x10⁻⁵
1.00x10⁻⁴
C (M)

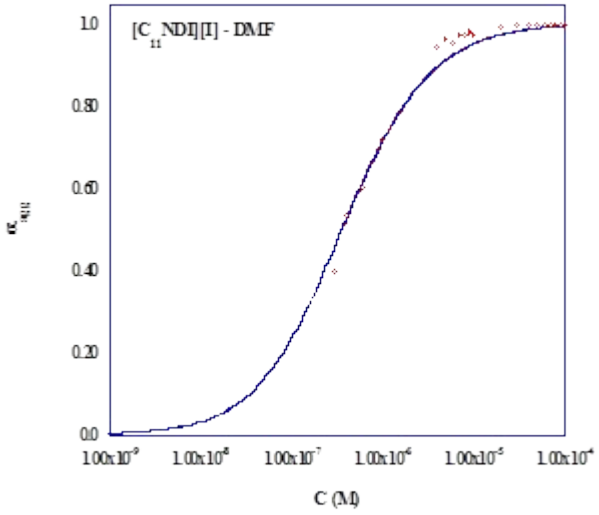

[C8NDI][I] - THF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁷
1.00x10⁻⁵
C (M)

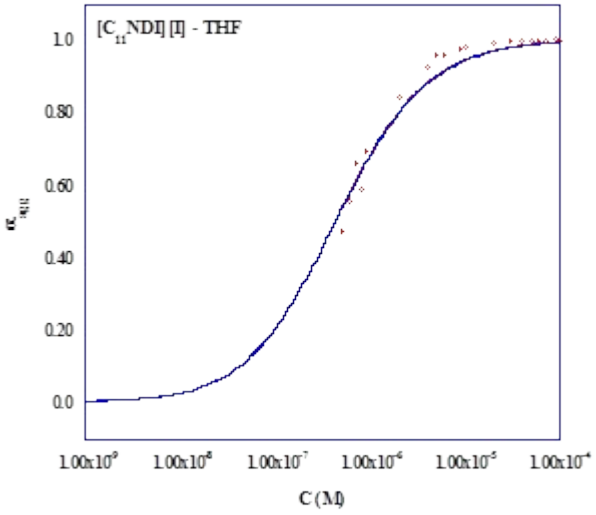

[C9NDI][I] - DMF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁷
1.00x10⁻⁵
C (M)

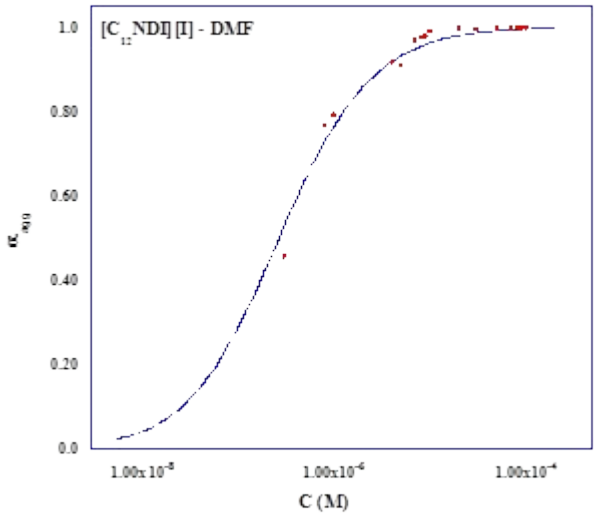

[C9NDI][I] - THF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁸
1.00x10⁻⁷
1.00x10⁻⁶
1.00x10⁻⁵
0.000100
C (M)

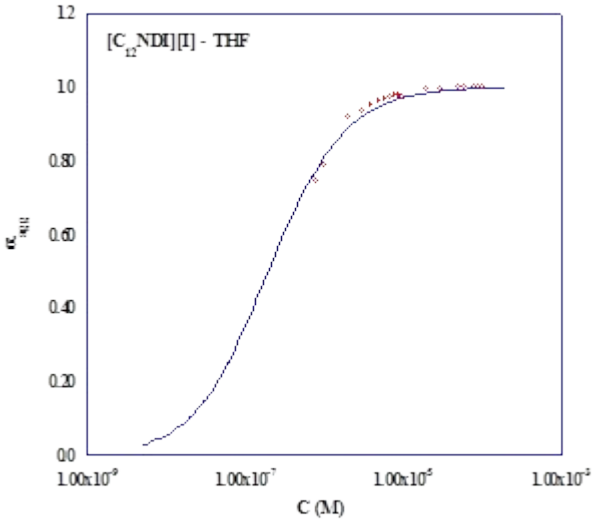

[C10NDI][I] - DMF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁷
1.00x10⁻⁵
C (M)


[C10NDI][I] - THF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁸
1.00x10⁻⁷
1.00x10⁻⁶
1.00x10⁻⁵
1.00x10⁻⁴
C (M)


[C11NDI][I] - DMF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁸
1.00x10⁻⁷
1.00x10⁻⁶
1.00x10⁻⁵
1.00x10⁻⁴
C (M)


[C11NDI][I] - THF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁸
1.00x10⁻⁷
1.00x10⁻⁶
1.00x10⁻⁵
1.00x10⁻⁴
C (M)


[C12NDI][I] - DMF
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁸
1.00x10⁻⁶
1.00x10⁻⁴
C (M)


[C12NDI][I] - THF
1.2
1.0
0.80
0.60
0.40
0.20
0.0
1.00x10⁻⁹
1.00x10⁻⁷
1.00x10⁻⁵
1.00x10⁻³
C (M)

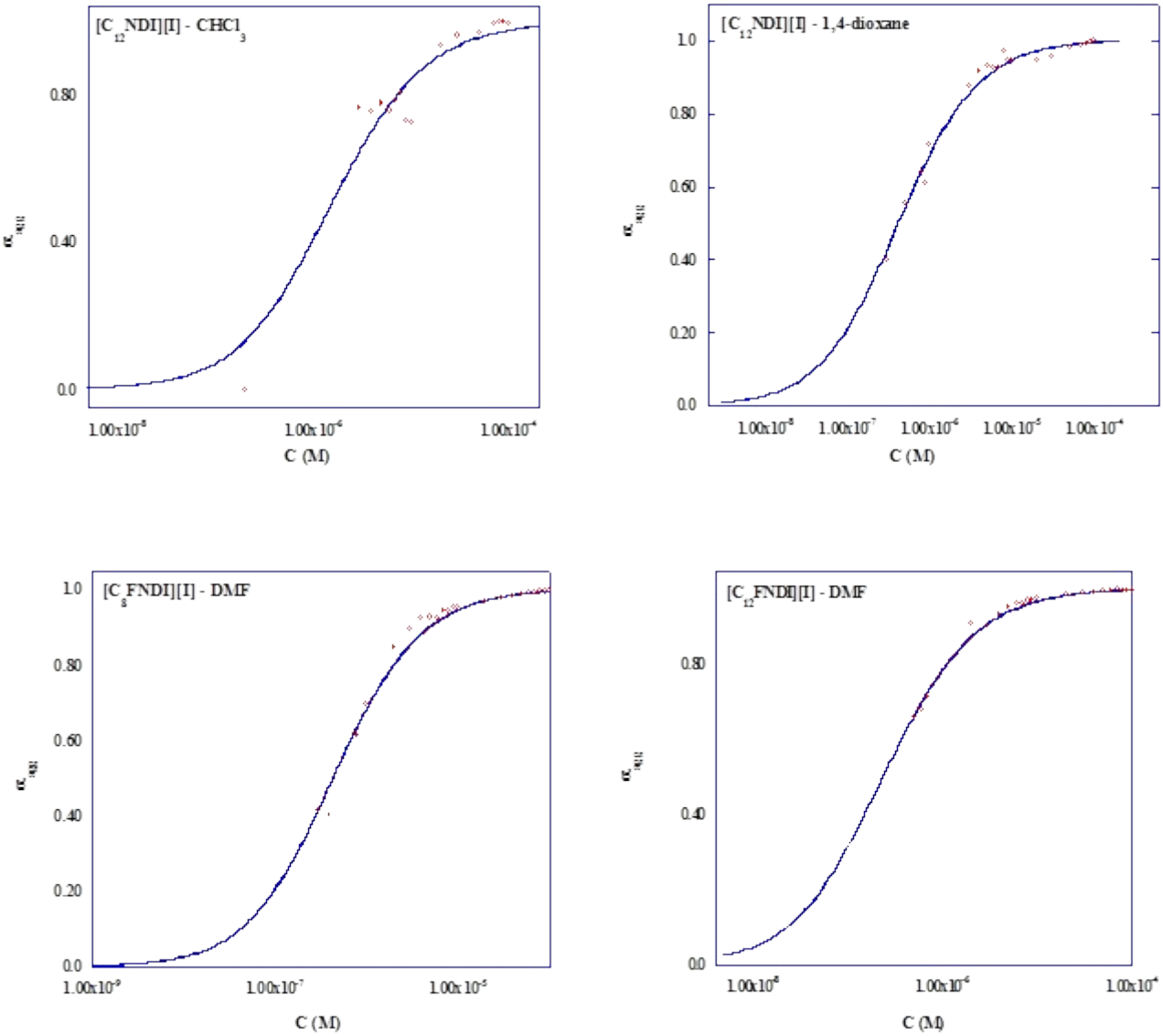
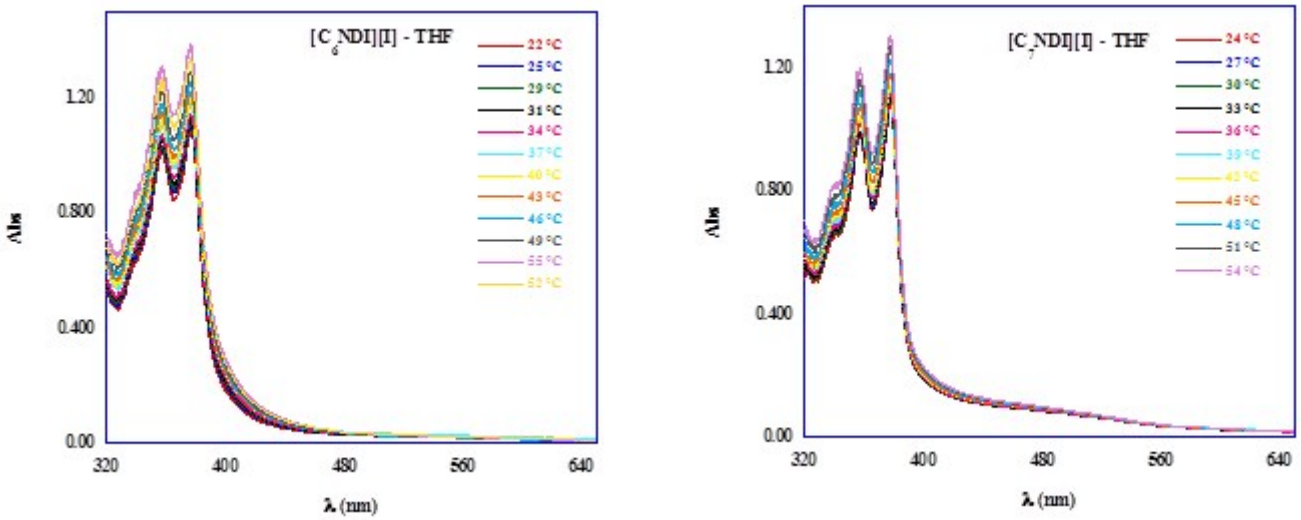


Figure S5. Plot of α_{agg}as a function of concentration and solvent. α_{agg} was determined at 415 nm for **[C_8NDI][I]** in DMF , **[C_{10}NDI][I]** in THF and DMF. $\alpha_{agg}$was determined at 533 nm for **[C_{12}NDI][I]** in dioxane, at 435 nm at **[C_{12}NDI][I]** in $CHCl_3$ and at 422 nm in all the other cases.



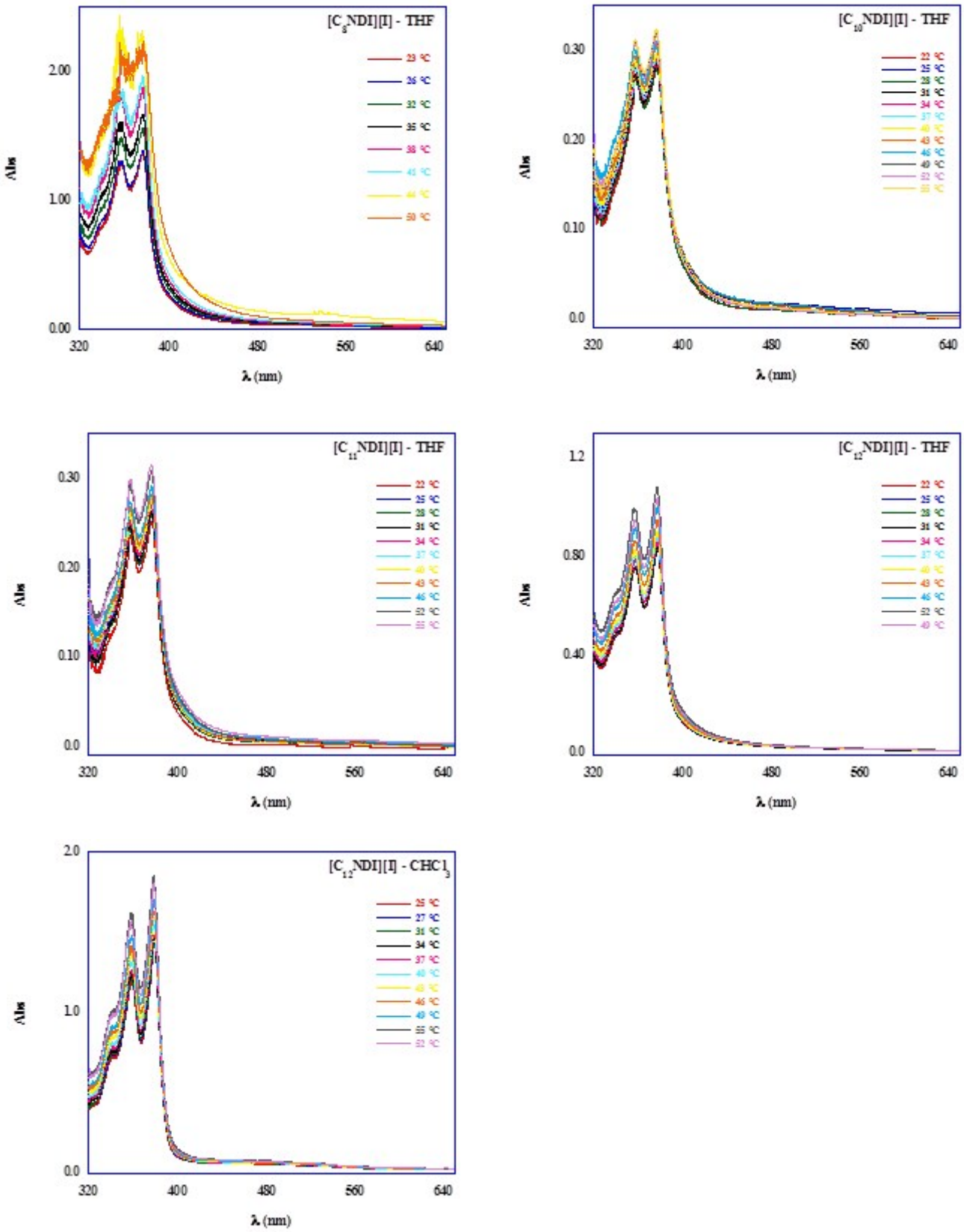
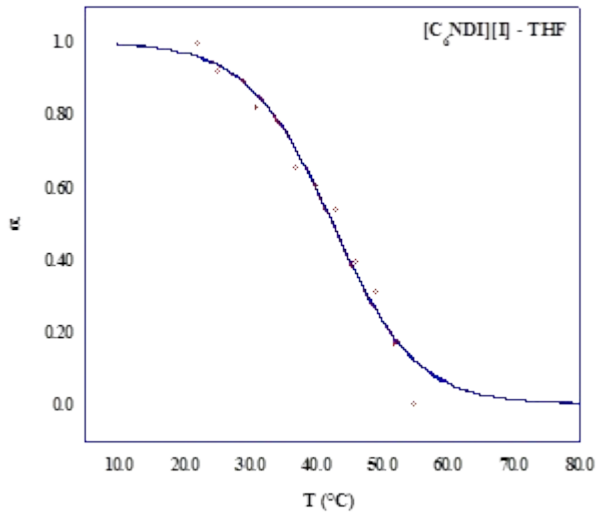
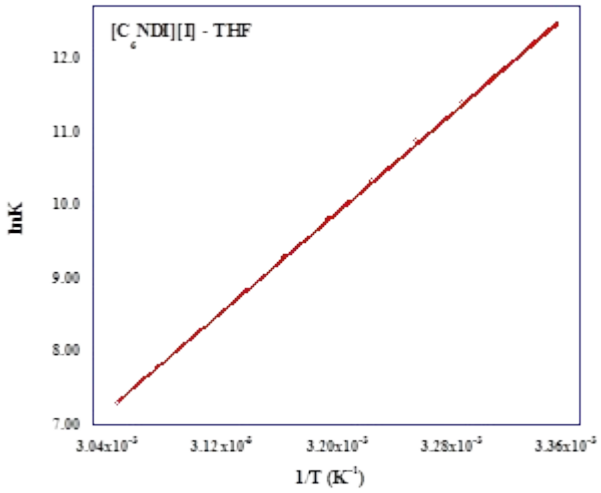
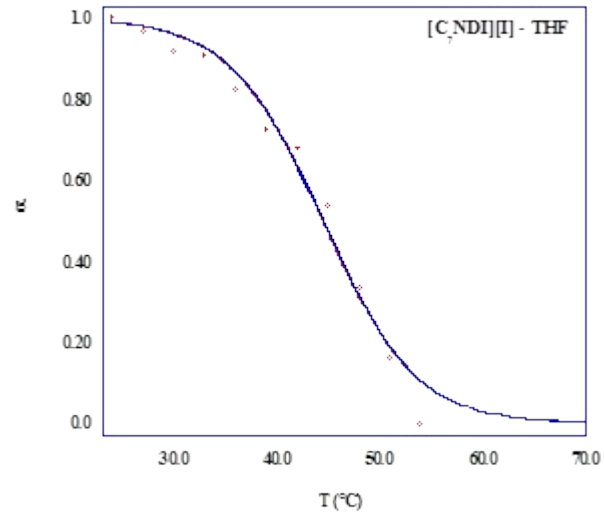
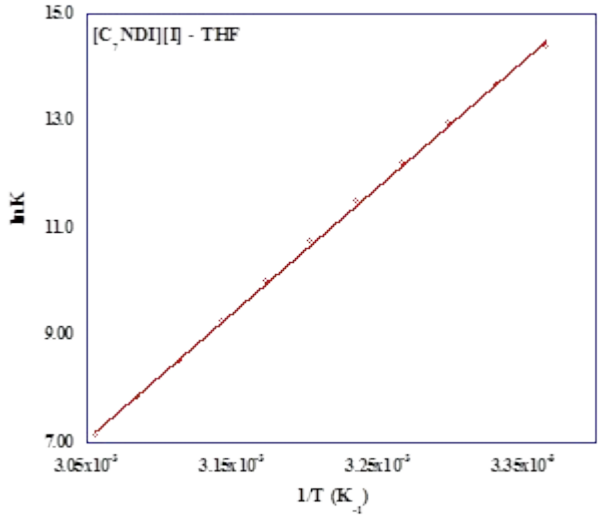


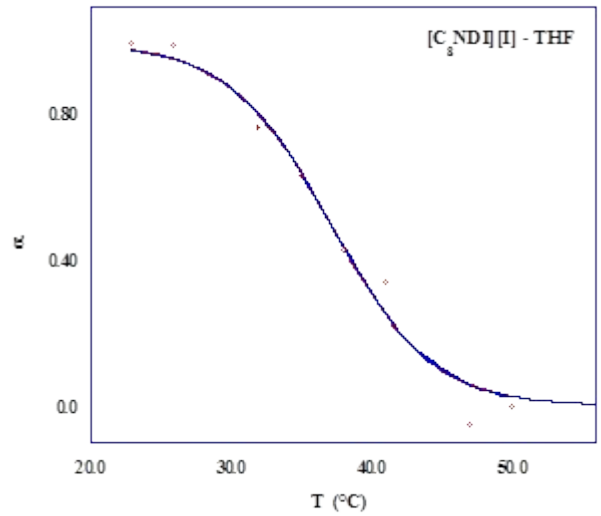
Figure S6. UV-vis spectra at fixed concentration ($5 \cdot 10^{-5}$ M) as a function of temperature.

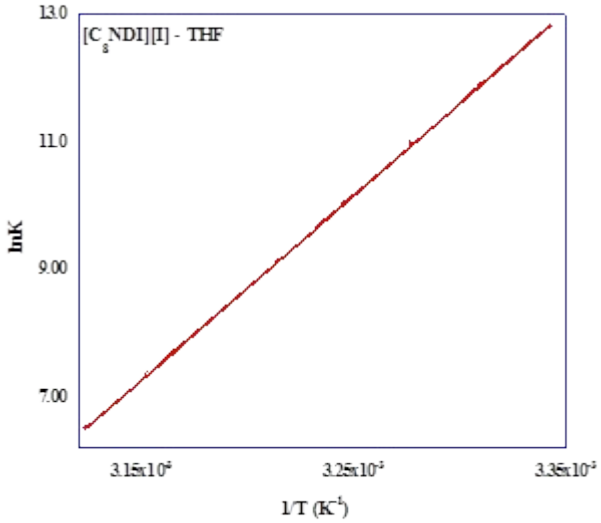

[C6NDI][I] - THF
α
T (°C)

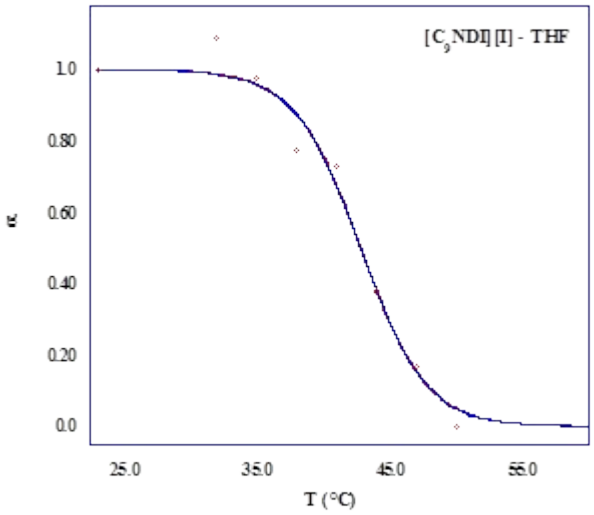

[C6NDI][I] - THF
lnK
1/T (K-1)

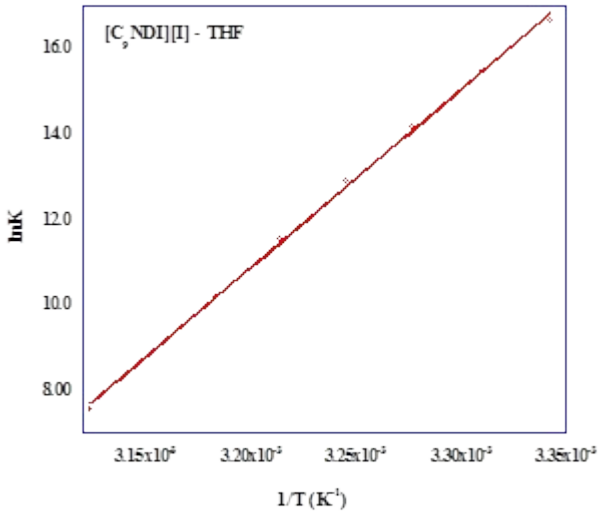

[C7NDI][I] - THF
α
T (°C)

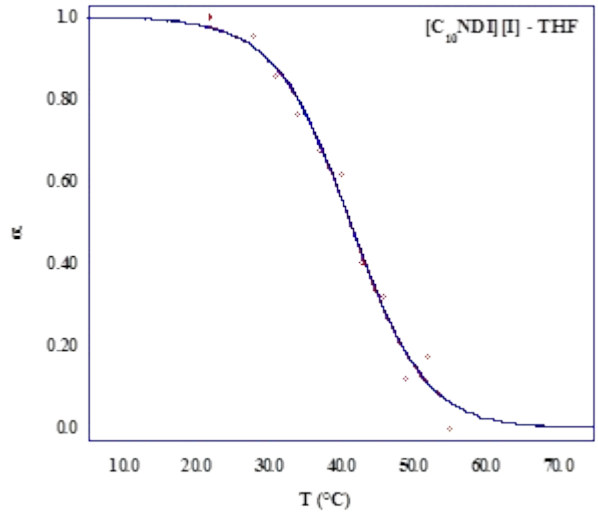

[C7NDI][I] - THF
lnK
1/T (K-1)

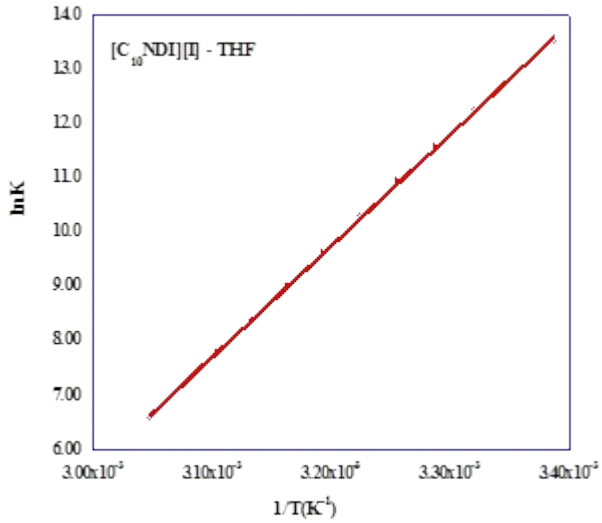

[C8NDI][I] - THF
α
T (°C)

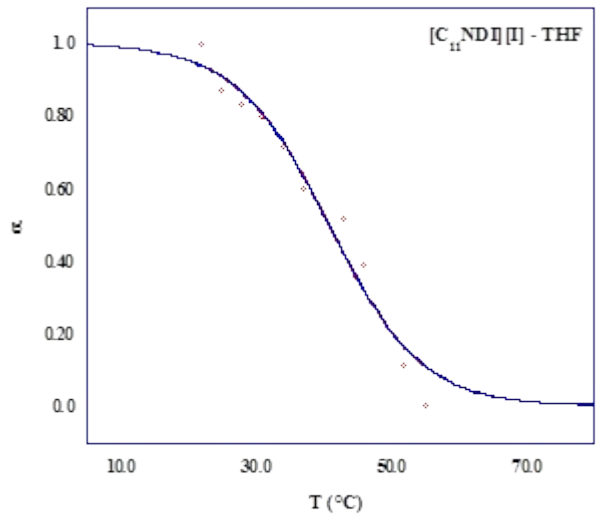

[C8NDI][I] - THF
lnK
1/T (K-1)

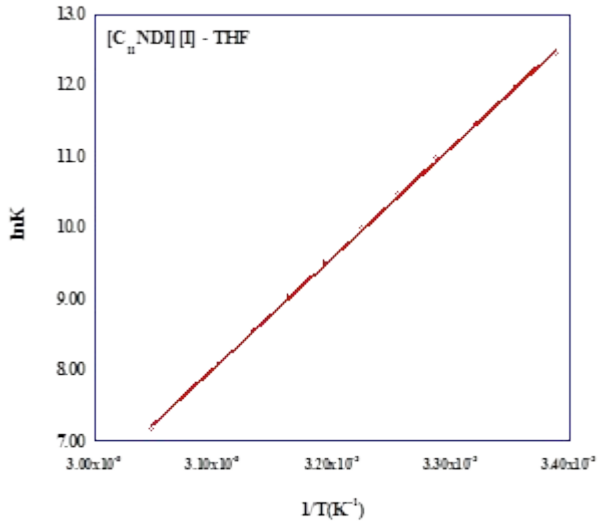

[C9NDI][I] - THF
α
T (°C)


[C9NDI][I] - THF
lnK
1/T (K-1)


[C10NDI][I] - THF
α
T (°C)


[C10NDI][I] - THF
lnK
1/T(K-1)


[C11NDI][I] - THF
α
T (°C)


[C11NDI][I] - THF
lnK
1/T(K-1)

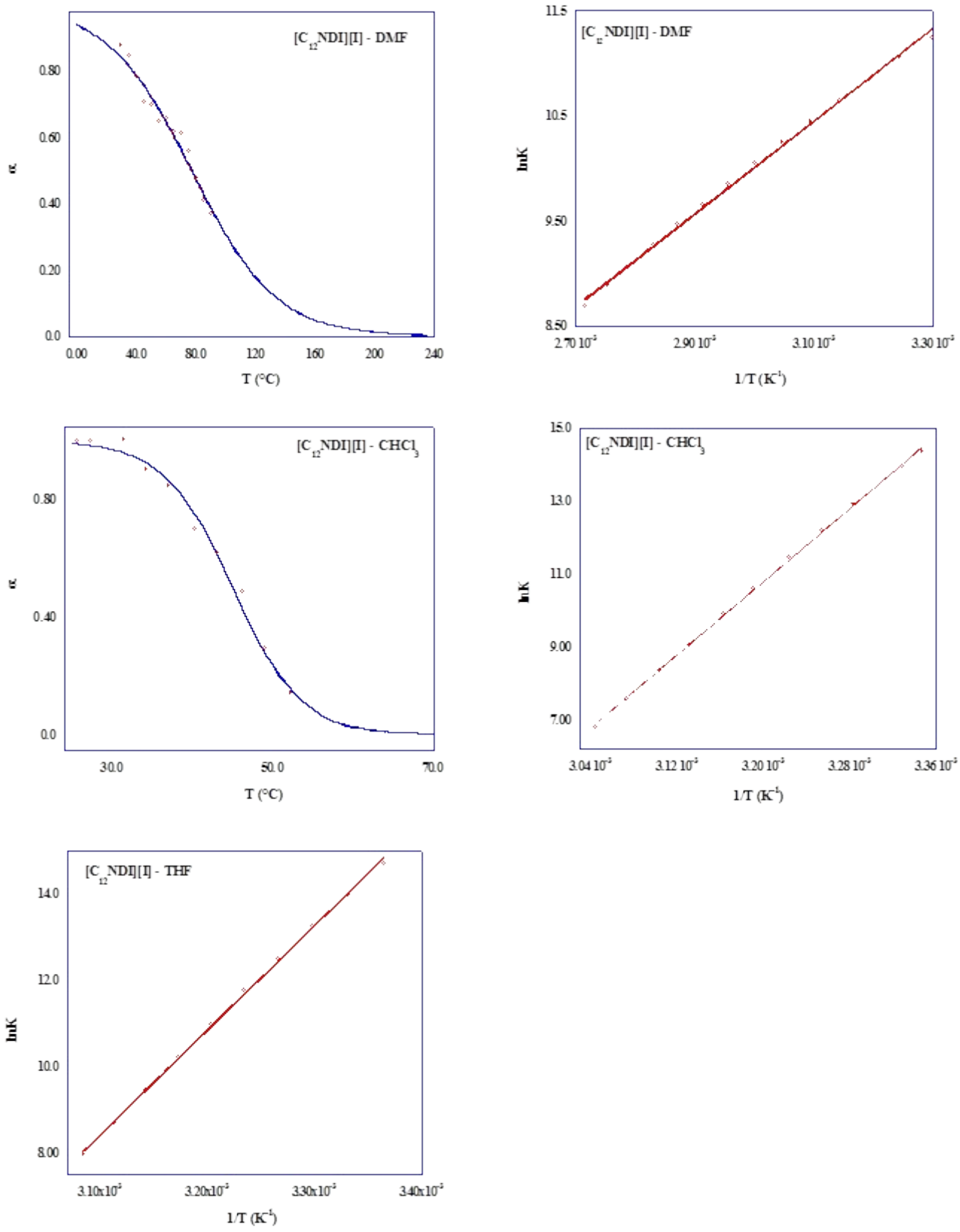


Figure S7. α and van't Hoff plots of UV-vis analysis at variable temperature and fixed concentration ($5 \cdot 10^{-5}$ M). α_{agg} was determined at 382 nm for **[C_6NDI][I],** at 380 nm for **[C_7NDI][I],** at 375 nm for **[C_8NDI][I],** at 377 for **[C_9NDI][I],** at 375 nm for **[C_{10}NDI][I]** and at 374 nm **[C_{11}NDI][I].**

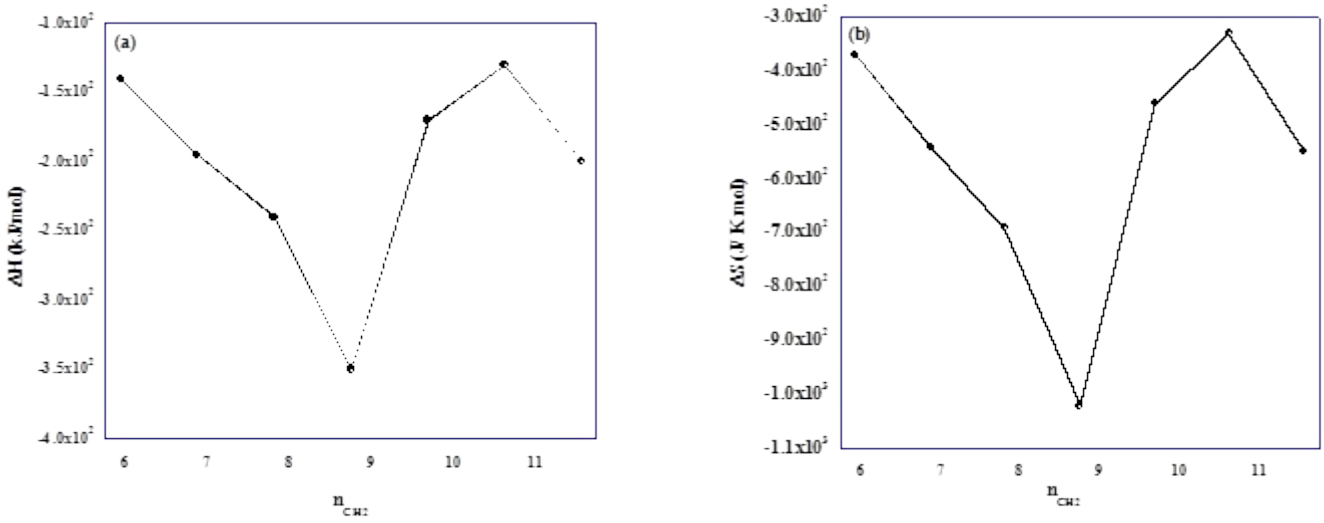
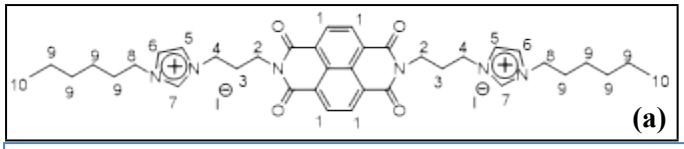
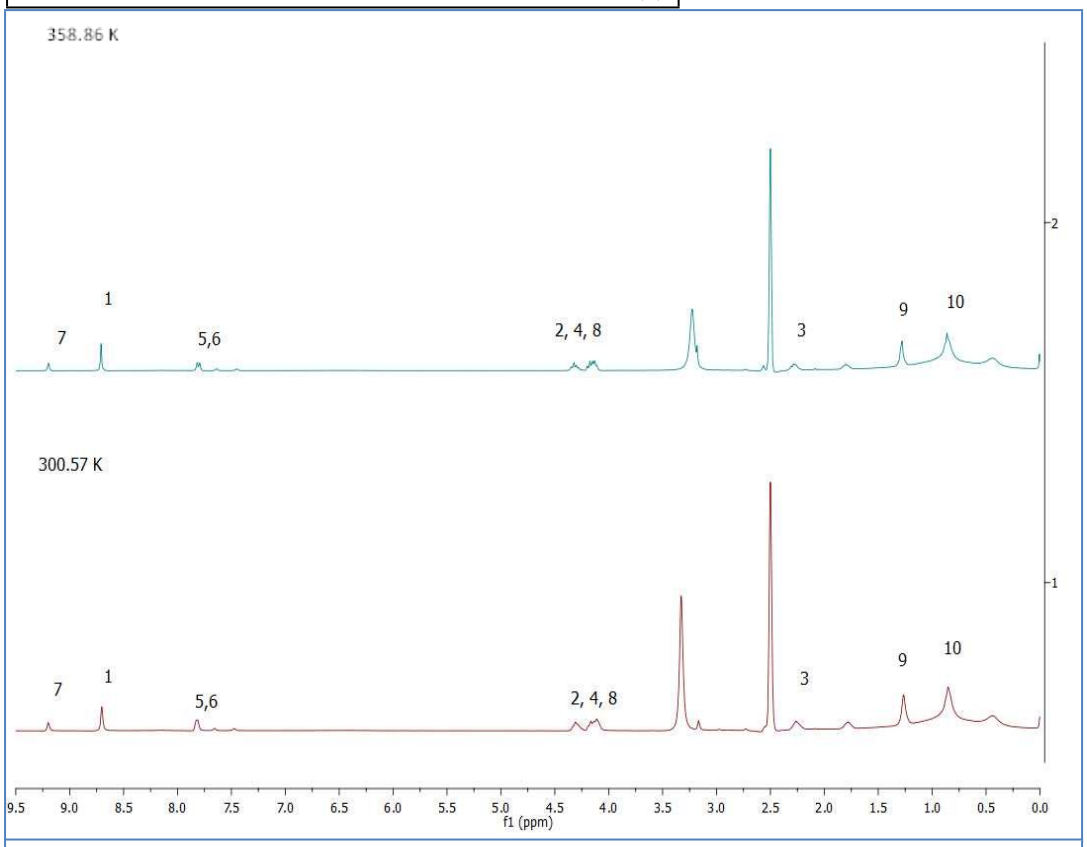
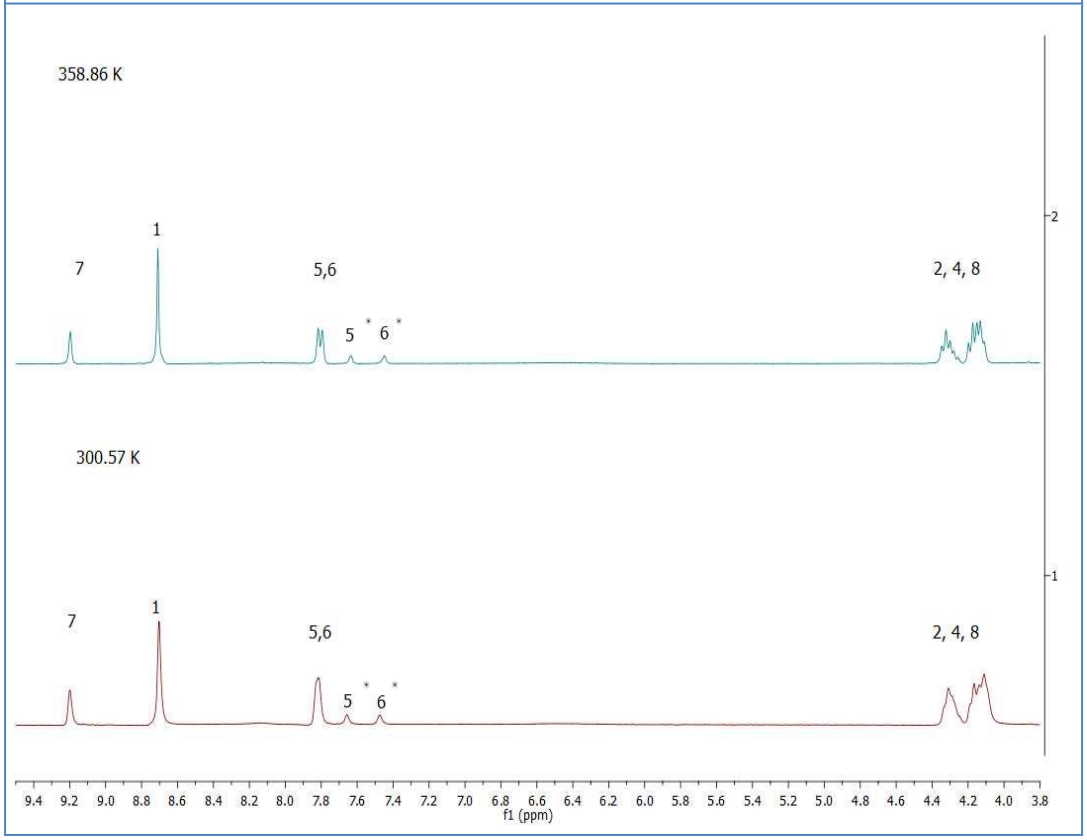
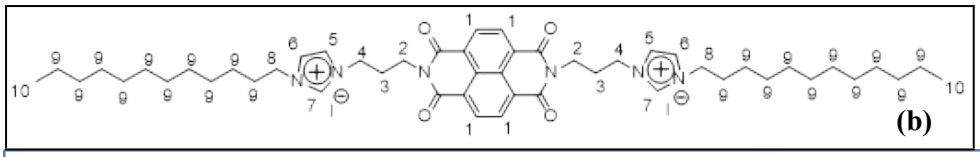


Figure S8. Plots of (**a**) Δ*H* and (**b**) Δ*S* as a function of the alkyl chain length.

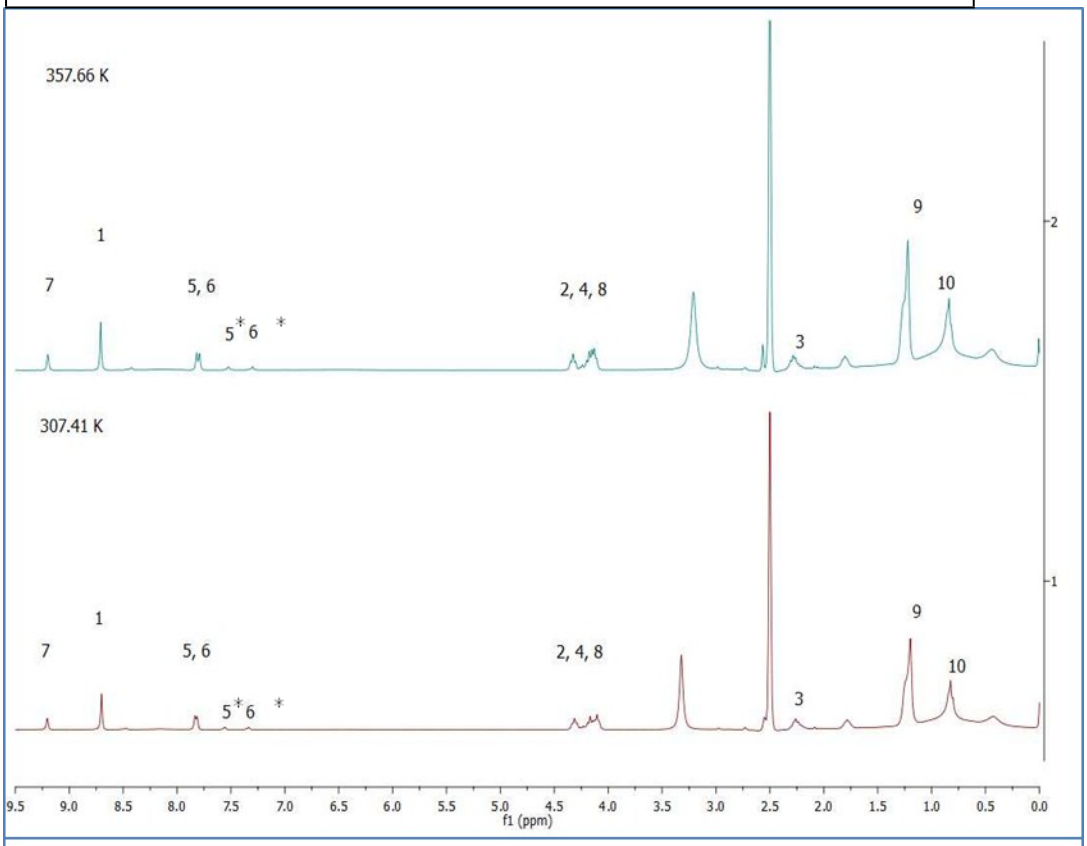

(a)

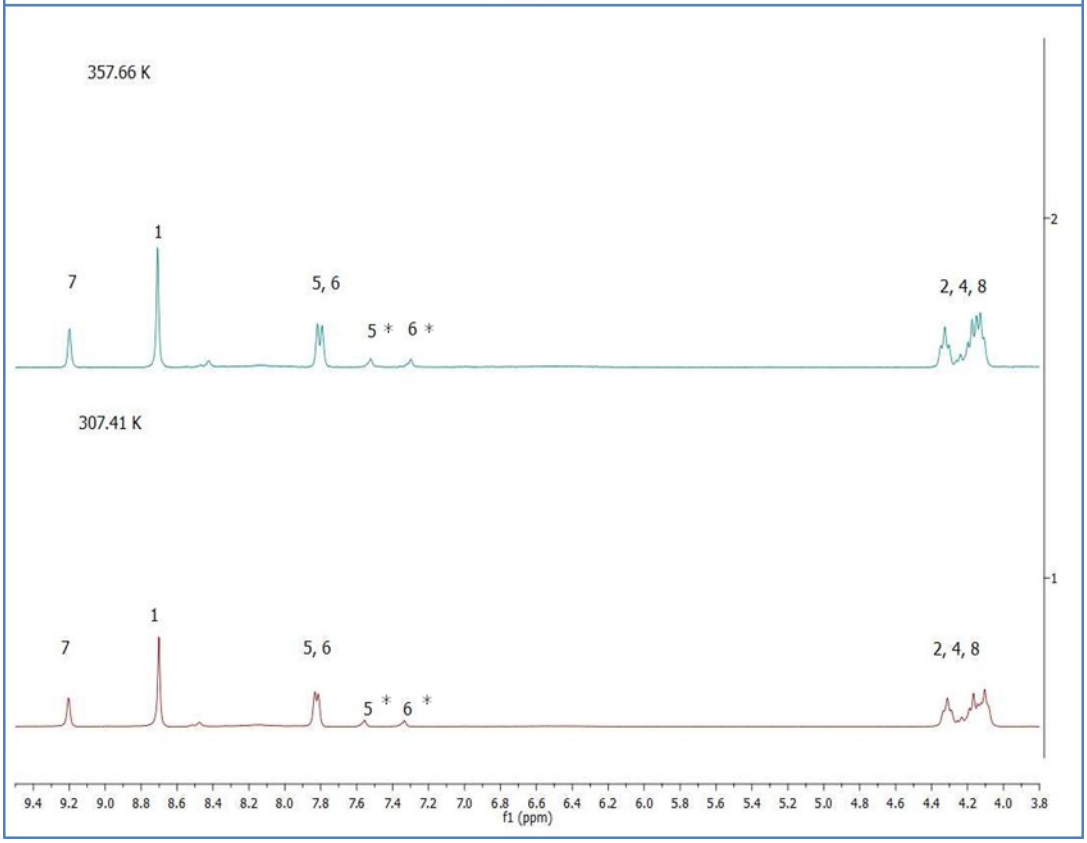

358.86 K
7
1
5,6
2, 4, 8
3
9
10
300.57 K
7
1
5,6
2, 4, 8
3
9
10
f1 (ppm)


358.86 K
7
1
5,6
5
6
2, 4, 8
300.57 K
7
1
5,6
5
6
2, 4, 8
f1 (ppm)



(b)


357.66 K
1
7
5, 6
5 * 6 *
2, 4, 8
3
9
10
2
307.41 K
1
7
5, 6
5 * 6 *
2, 4, 8
3
9
10
1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


357.66 K
1
7
5, 6
5 * 6 *
2, 4, 8
2
307.41 K
1
7
5, 6
5 * 6 *
2, 4, 8
1
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
f1 (ppm)

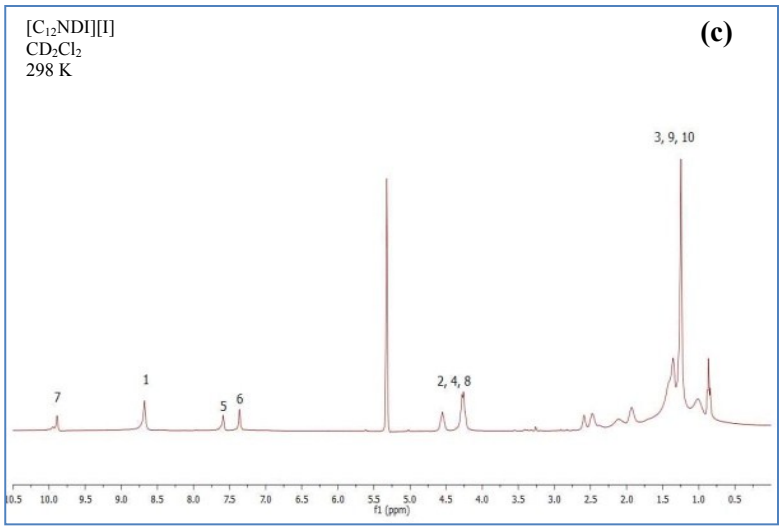
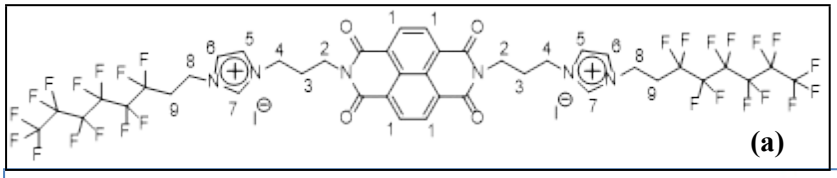
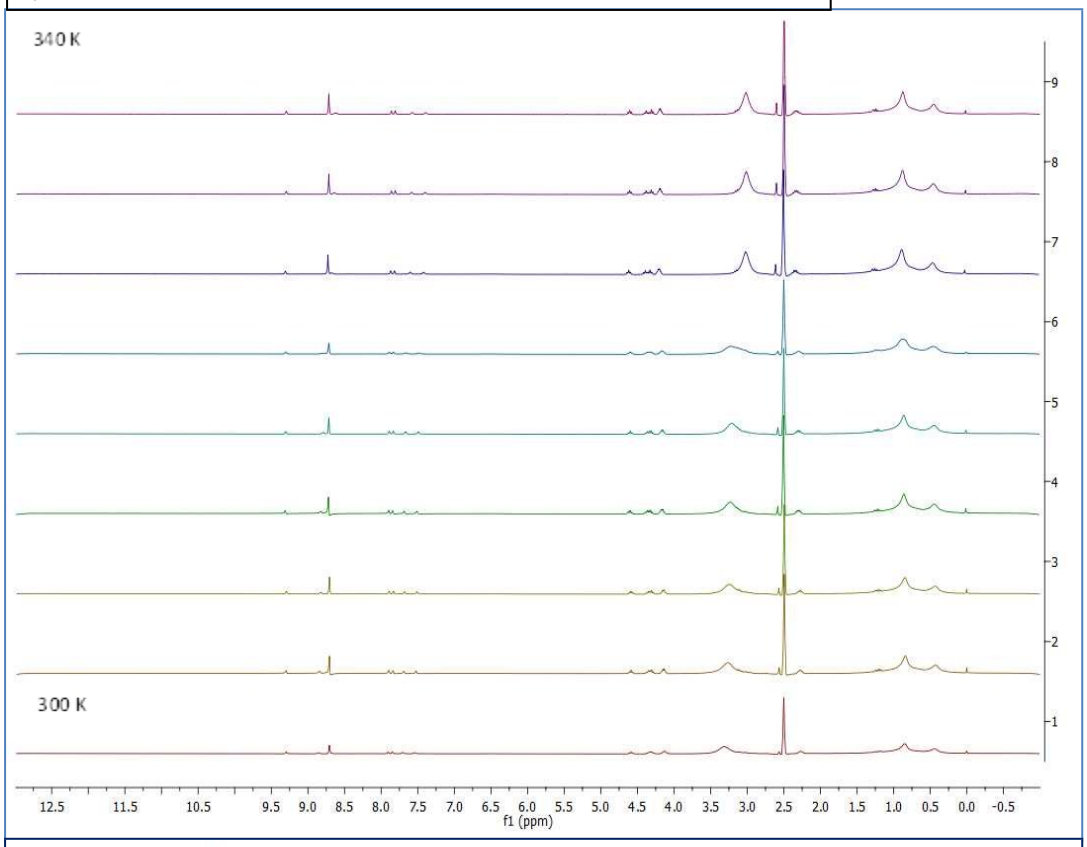
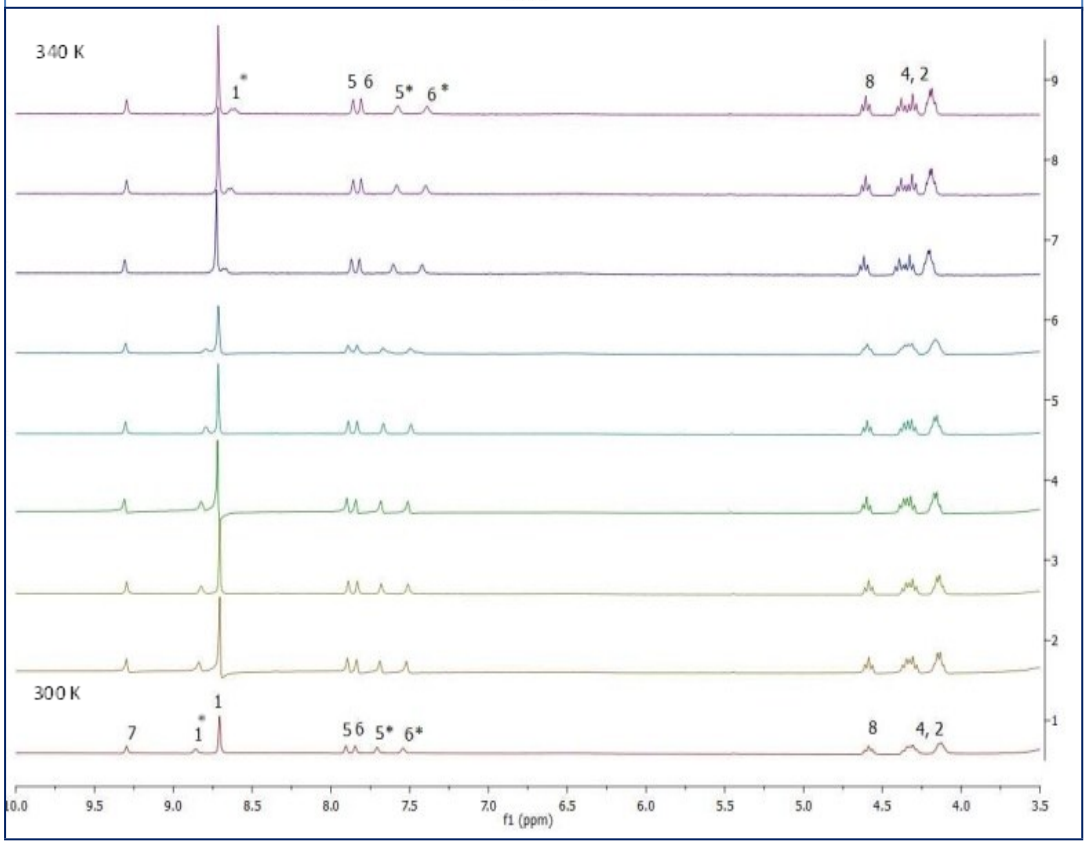


Figure S9. ^{1}H NMR spectra at variable temperature of **(a)[C_6NDI][I]** in DMSO-[d_6], **(b)[C_{12}NDI][I]** in DMSO-[d_6] and **(c)[C_{12}NDI][I]** in CD_2Cl_2-[d_2] respectively.



(a)





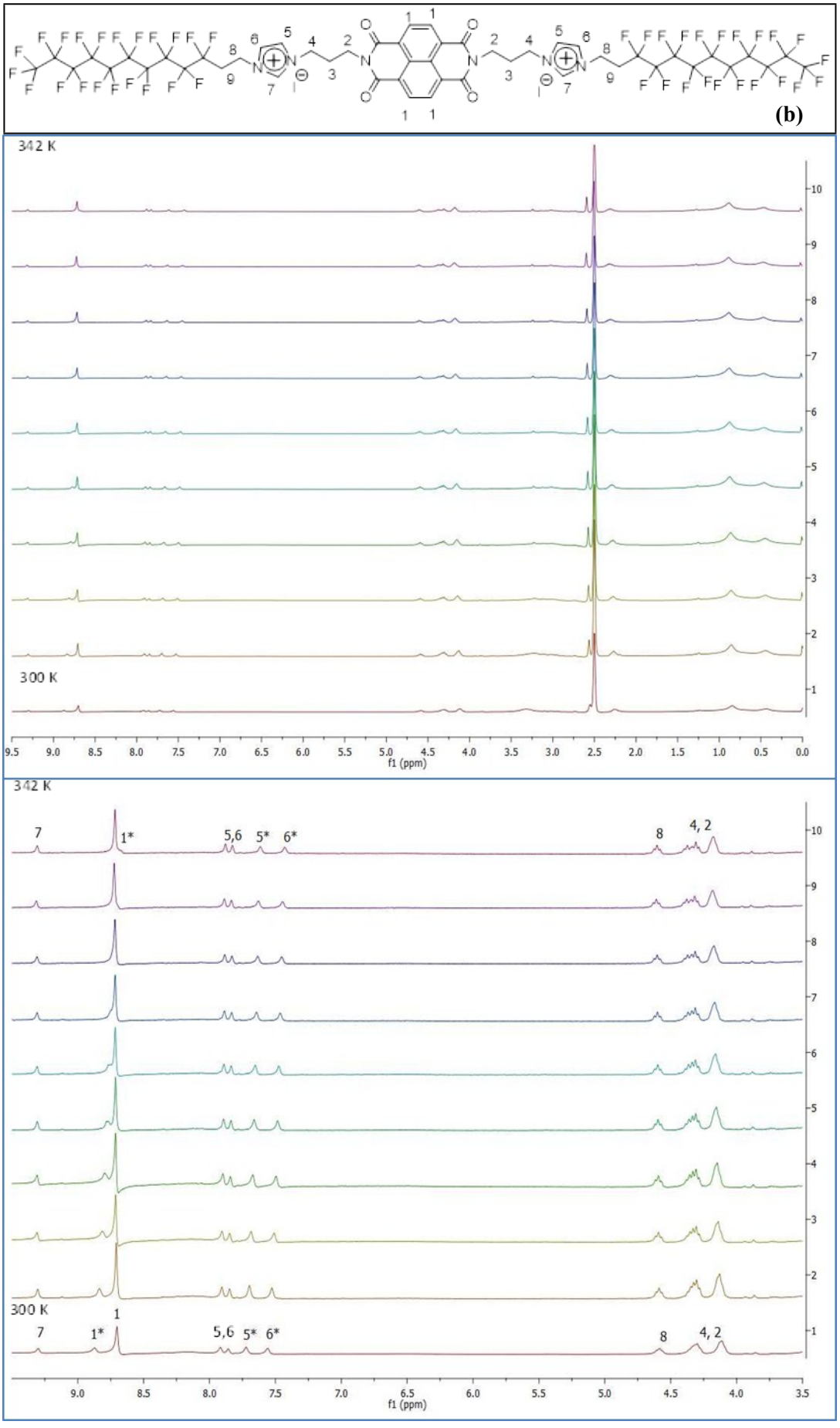
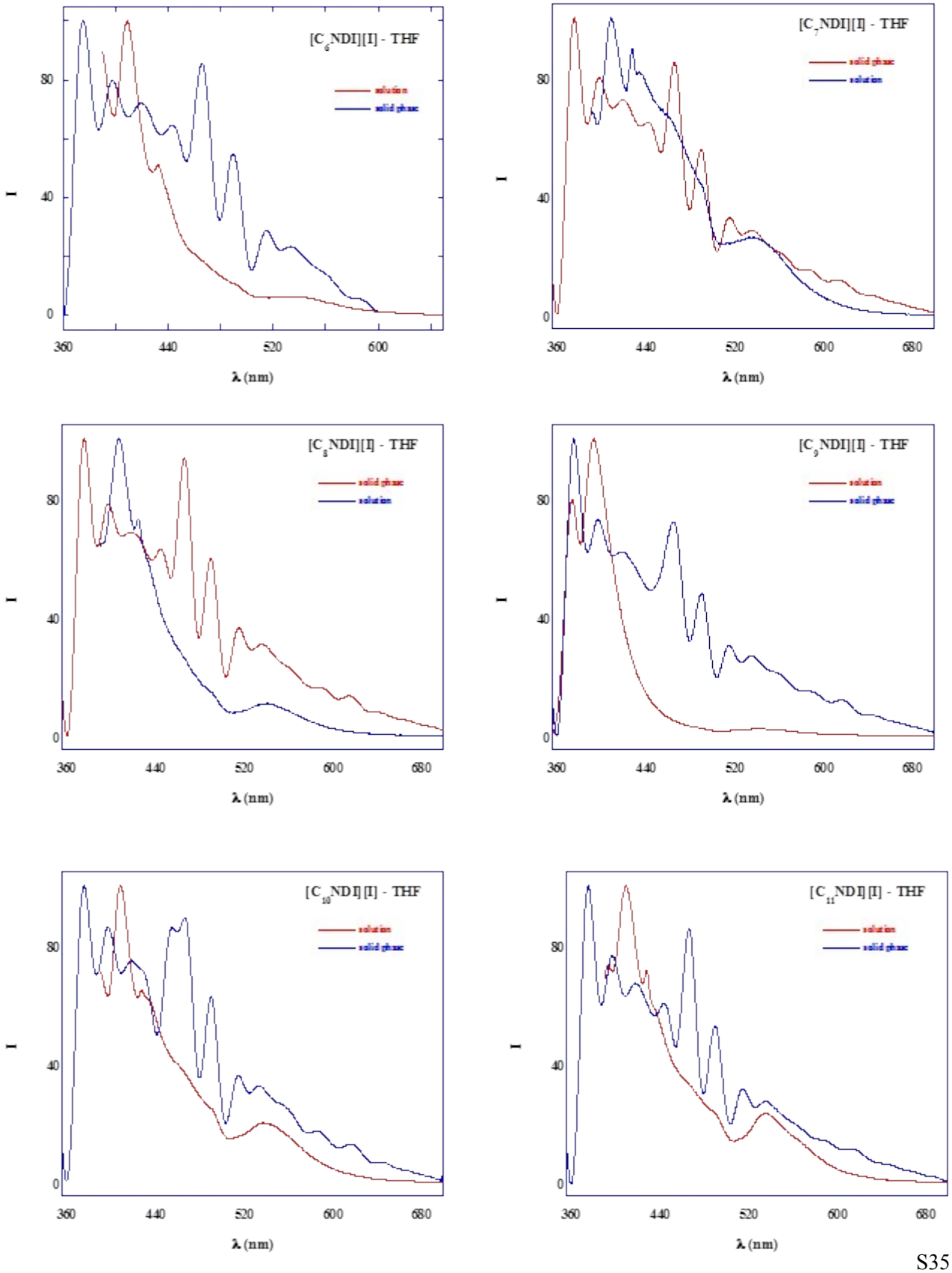

(b)
342 K
300 K
f1 (ppm)
342 K
7
1*
5,6
5*
6*
8
4, 2
300 K
1
f1 (ppm)

Figure S10. ^{1}H NMR spectra at variable temperature of **(a)[C_8FNDI][I]** in DMSO-[d_6] and **(b)[C_{12}FNDI][I]** in DMSO-[d_6] respectively.



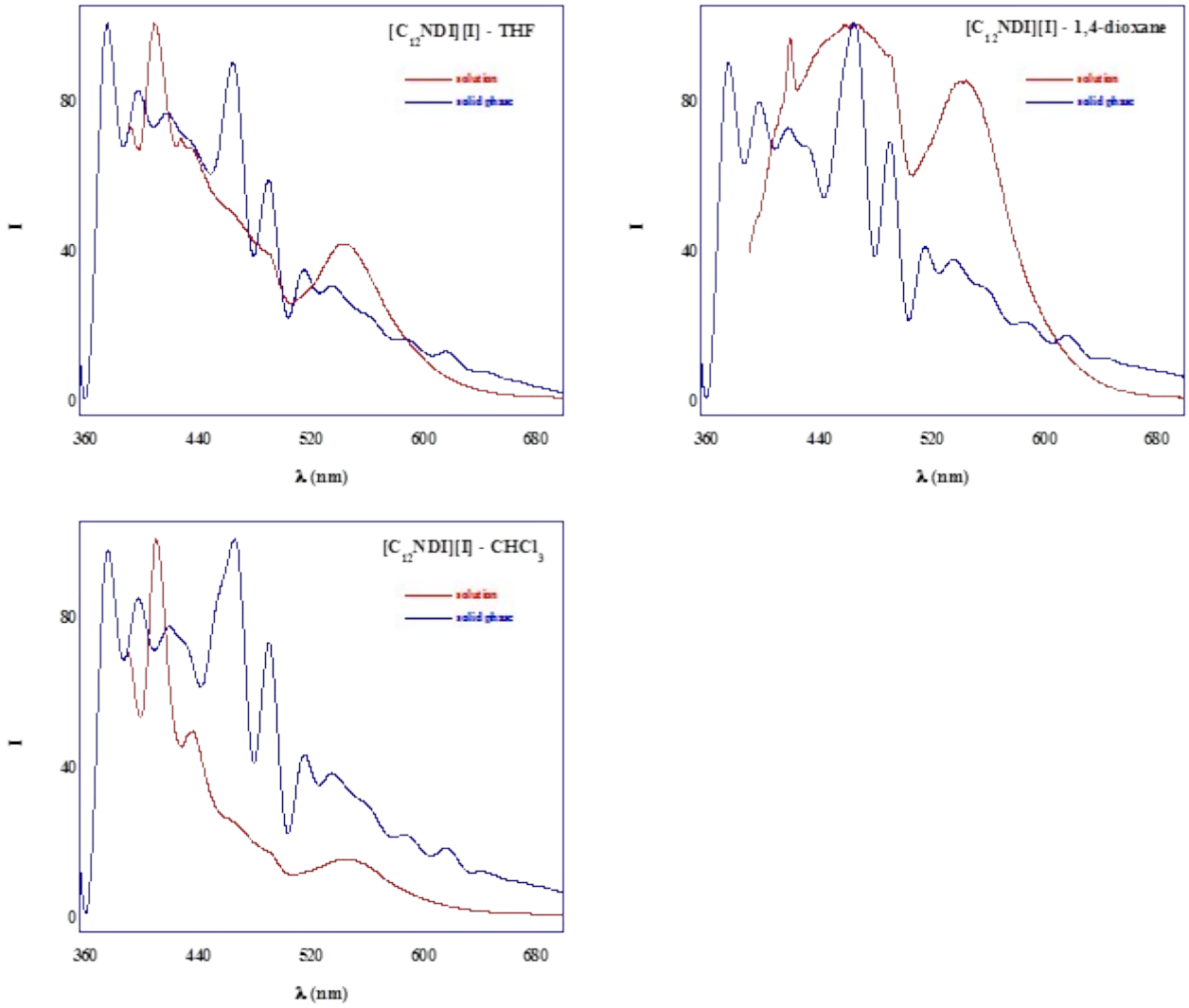


Figure S11. Fluorescent spectra in solution and in solid phase of salts. Fluorescence intensities are in arbitrary units. Excitation wavelength for solid-phase spectra are: 275 nm for **[C_6NDI][I]**, 277 nm for **[C_7NDI][I]**, 272 nm for **[C_8NDI][I], [C_9NDI][I]**, and **[C_{10}NDI][I]**, 274 nm for **[C_{12}NDI][I]** deriving from drop-casting of solution in dioxane and chloroform. Excitation wavelength for solution-phase spectra are: 375 nm for **[C_6NDI][I]**, 380 nm for **[C_7NDI][I]**, 378 nm for **[C_8NDI][I],** 382 nm for **[C_9NDI][I]** and **[C_{10}NDI][I]**, 381 nm for **[C_{11}NDI][I]**, 380 nm for **[C_{12}NDI][I]** in dioxane and 383 nm for **[C_{12}NDI][I]** in chloroform.

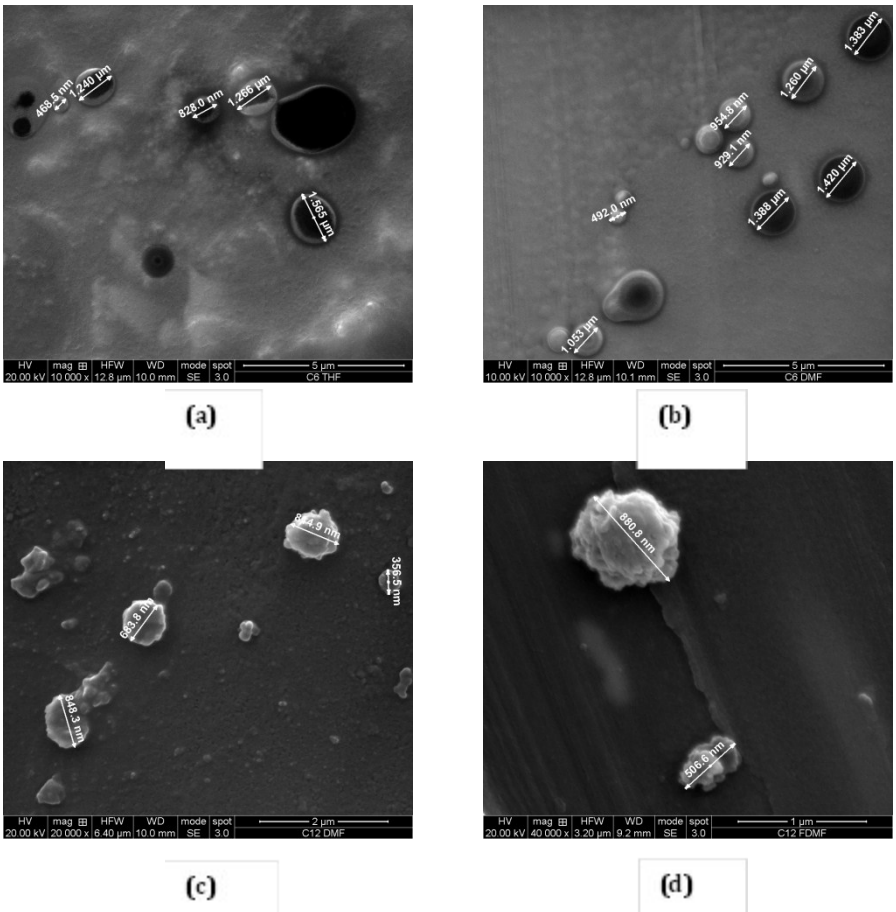
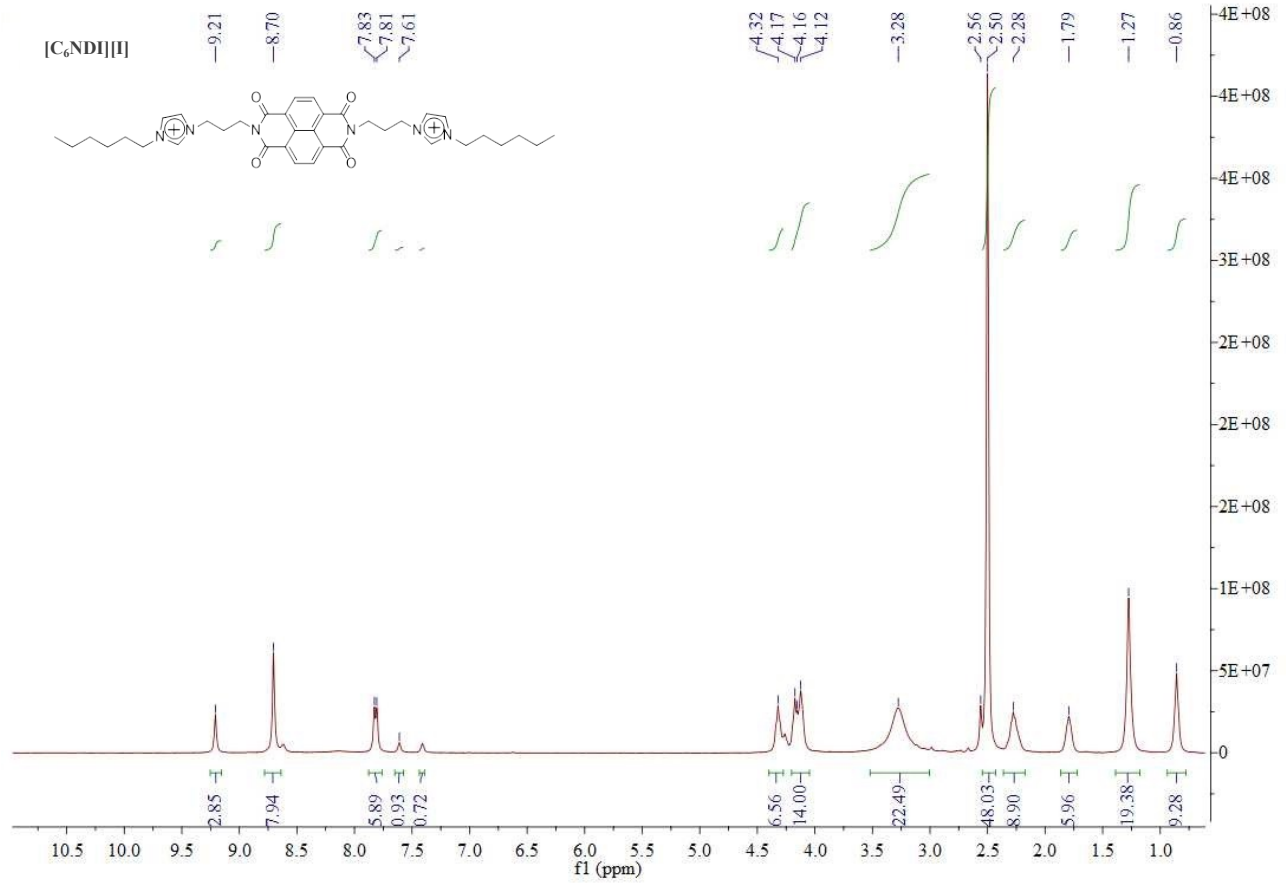
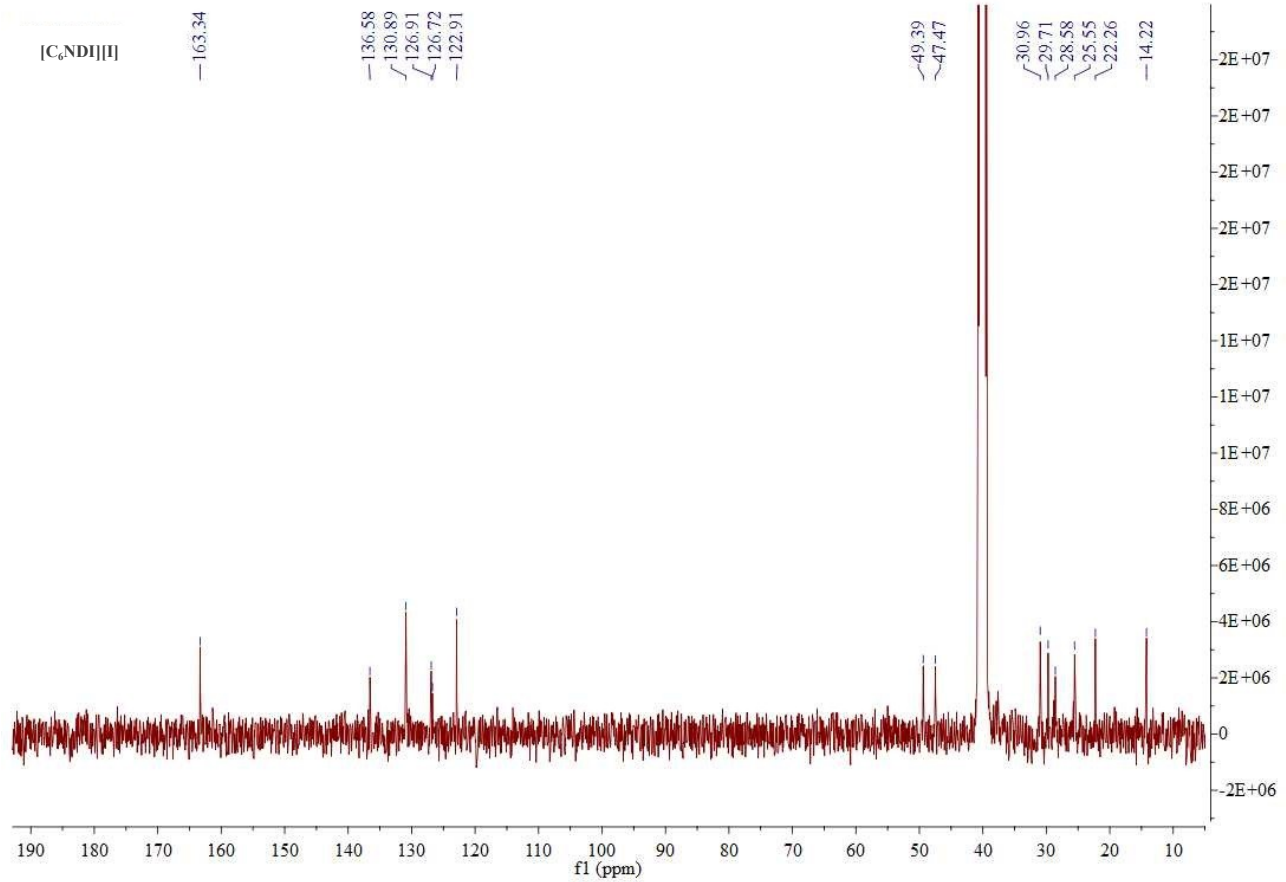
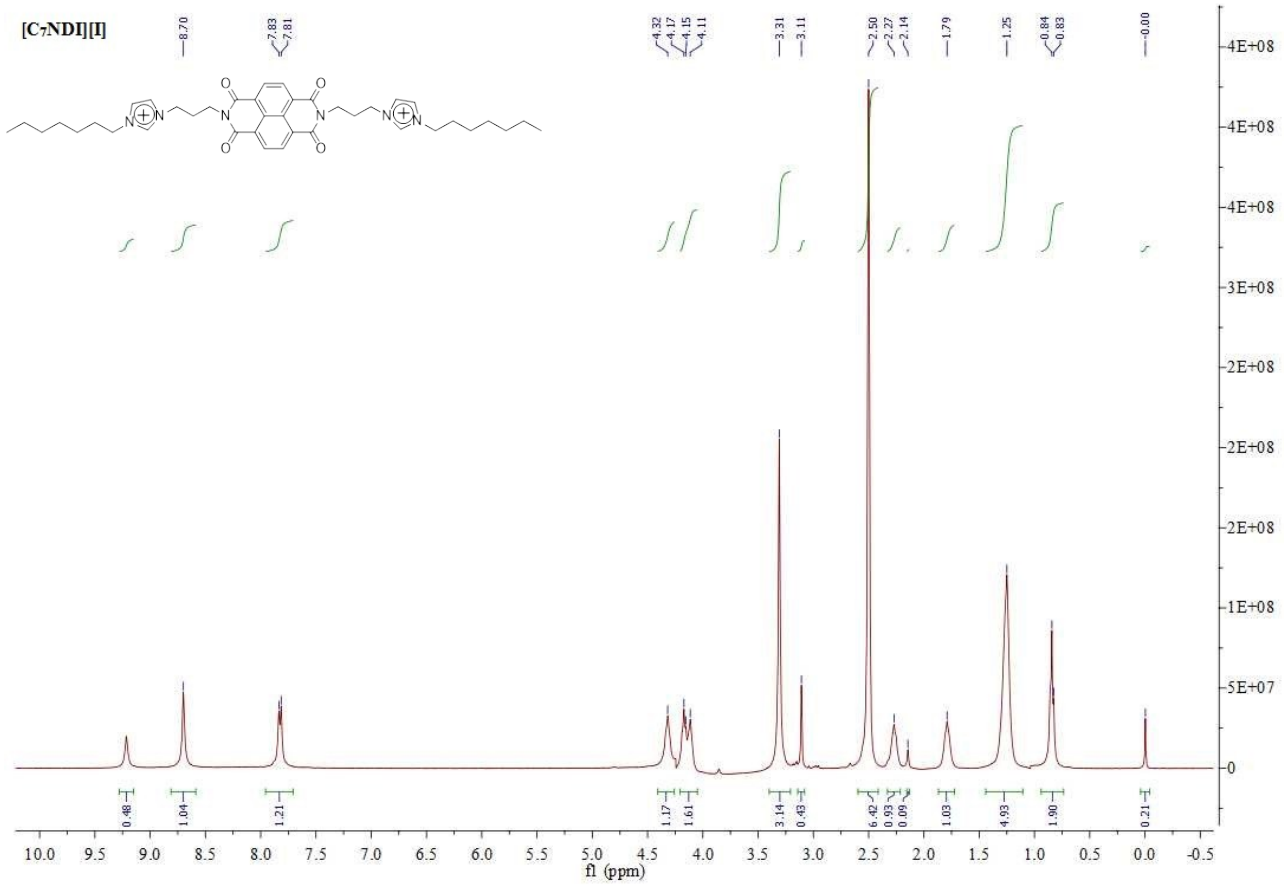
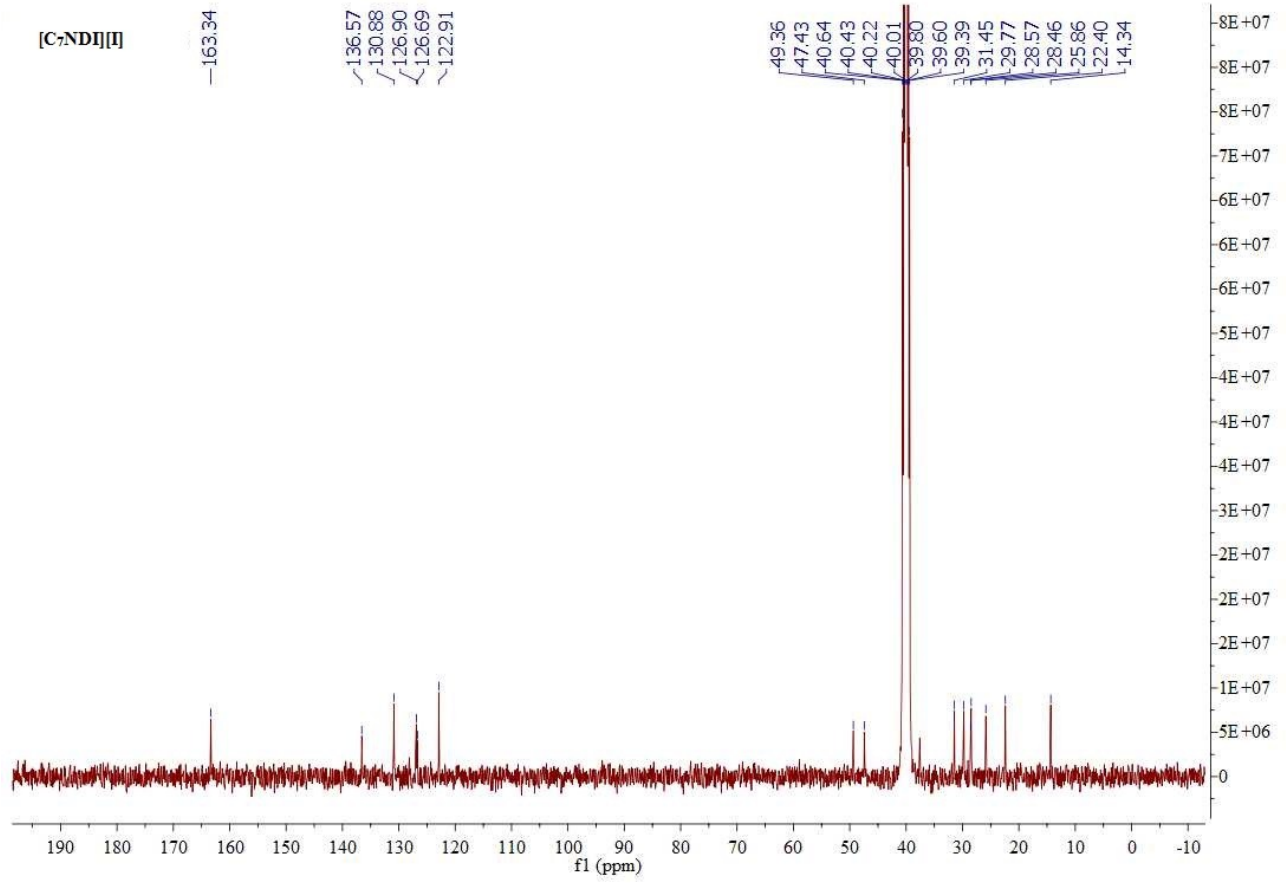


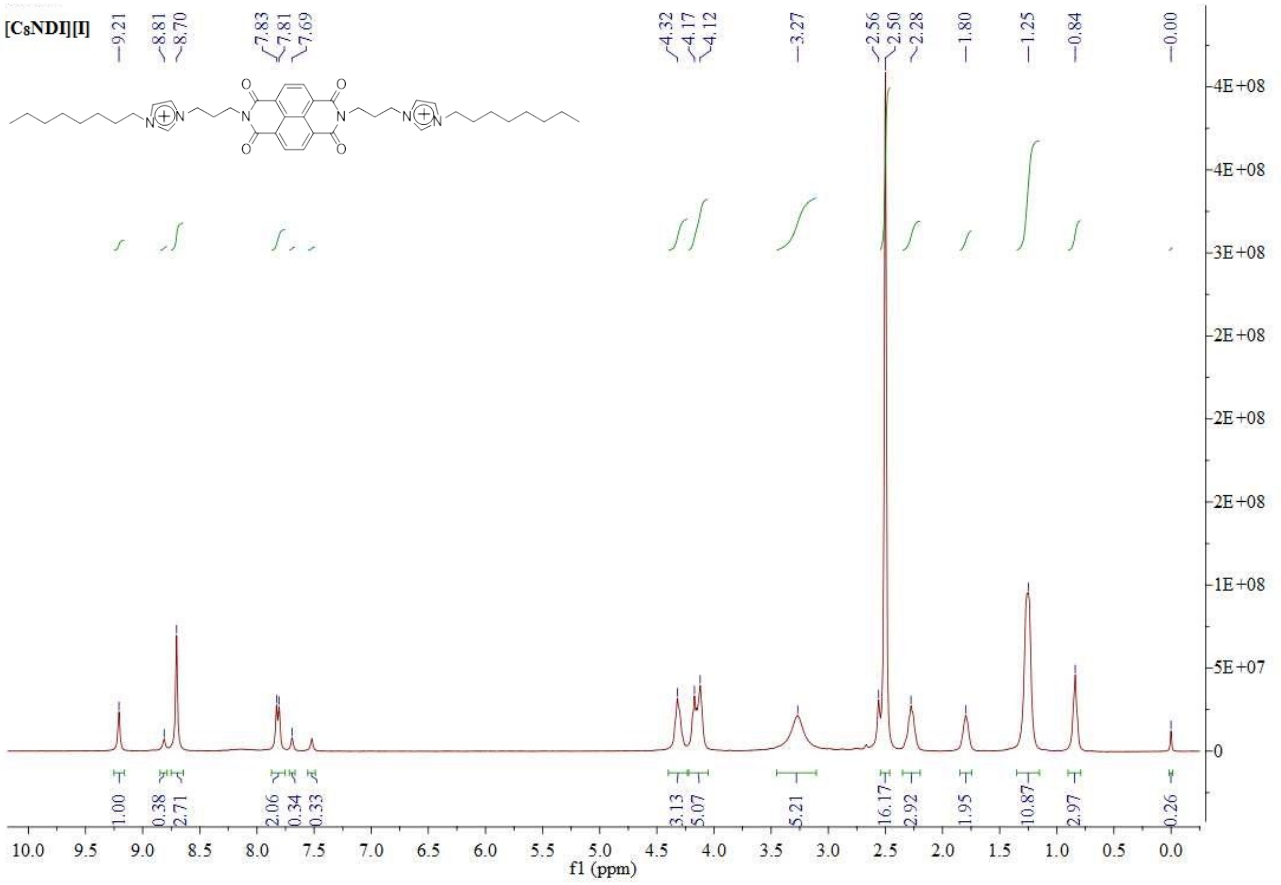
Figure S12. SEM images collected at $5 \cdot 10^{-5}$ M from casting of (**a**) **[C_6NDI][I]** in THF; (**b**) **[C_6NDI][I]** in DMF; (**c**) **[C_{12}NDI][I]** in DMF; (**d**) and (**e**) **[C_{12}FNDI][I]** in DMF.

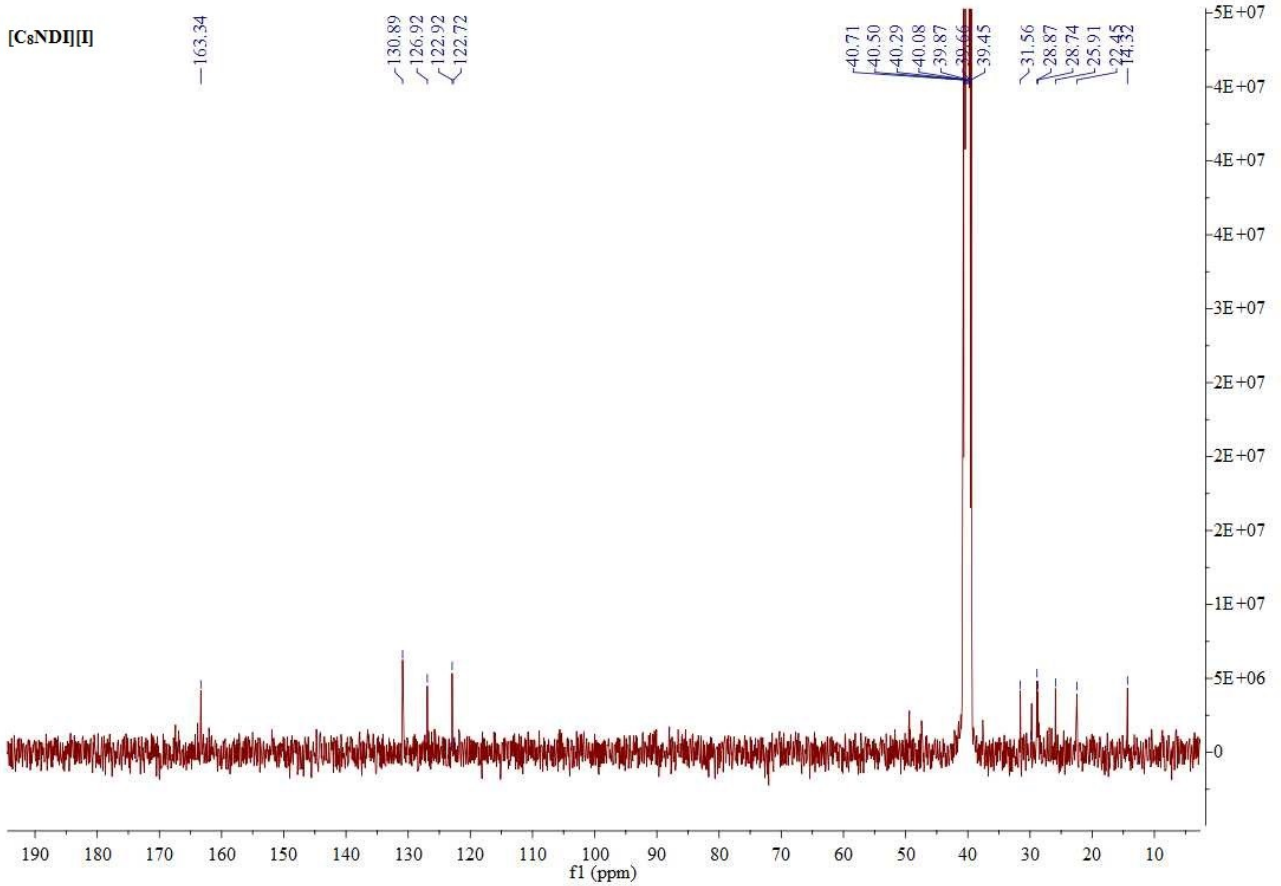

[C6NDI][I]
9.21
8.70
7.83
7.81
7.61
4.32
4.17
4.16
4.12
3.28
2.56
2.50
2.28
1.79
1.27
0.86
2.85
7.94
5.89
0.93
0.72
6.56
14.00
22.49
48.03
8.90
5.96
19.38
9.28
f1 (ppm)

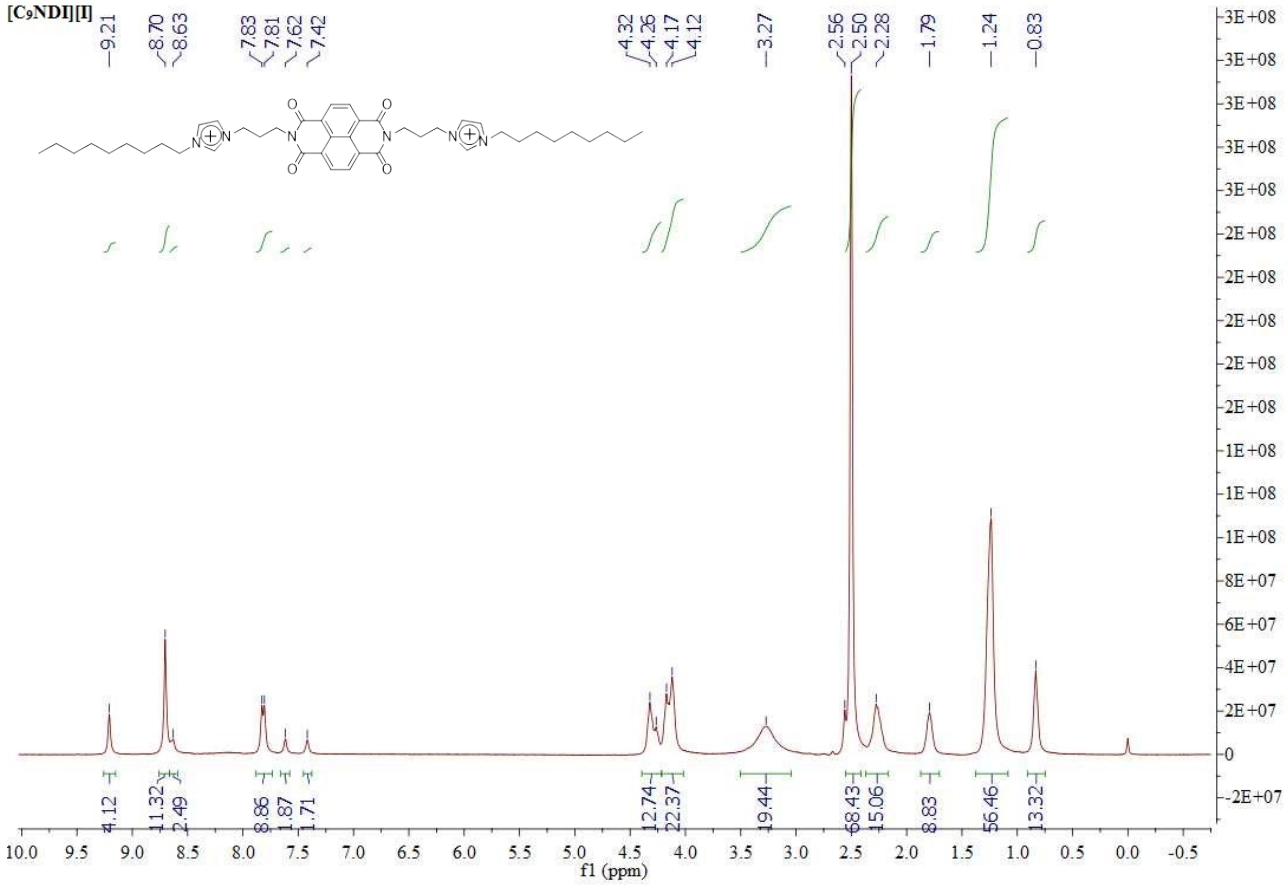

[C6NDI][I]
163.34
136.58
130.89
126.91
126.72
122.91
49.39
47.47
30.96
29.71
28.58
25.55
22.26
14.22
f1 (ppm)

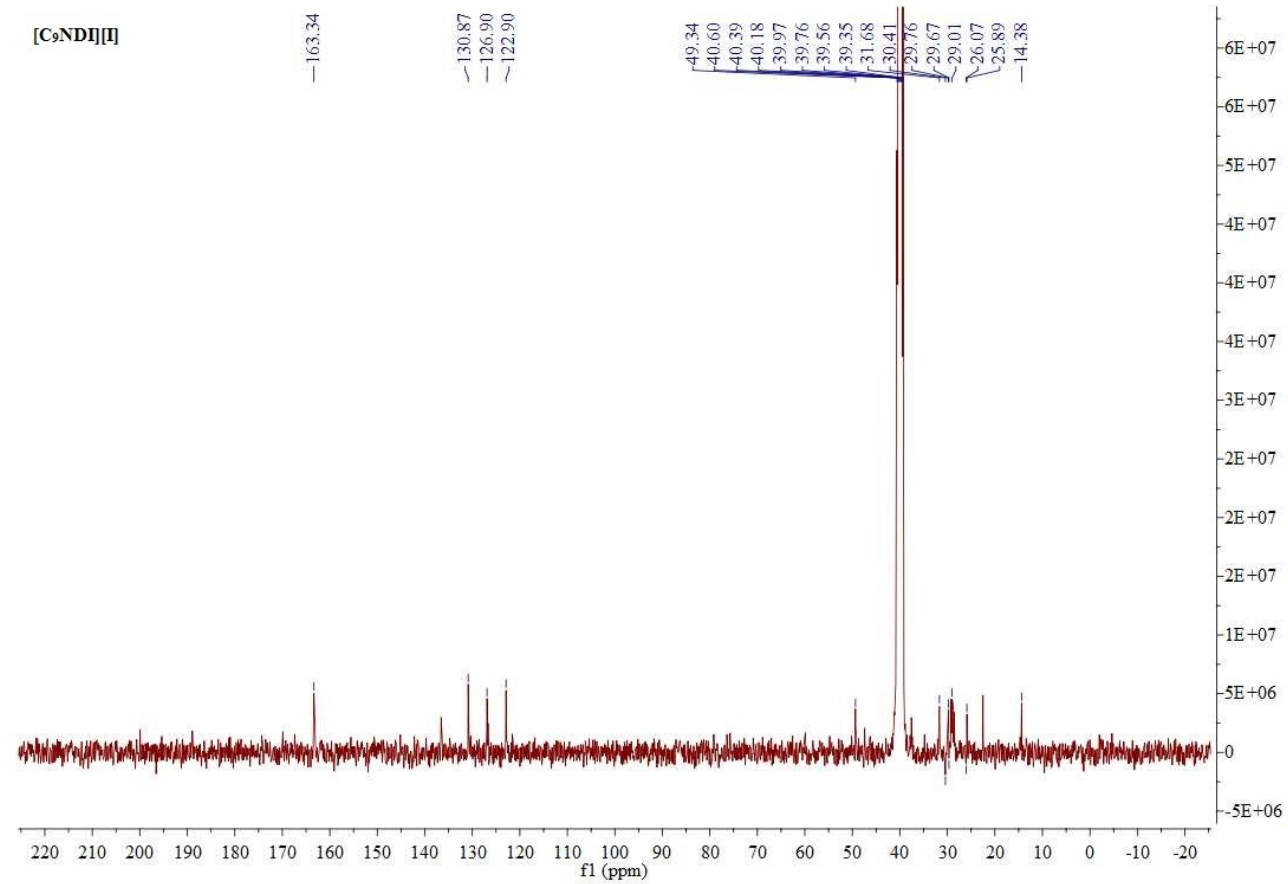

[C7NDI][I]
8.70
7.83
7.81
4.32
4.17
4.15
4.11
3.31
3.11
2.50
2.27
2.14
1.79
1.25
0.84
0.83
0.00
0.48
1.04
1.21
1.17
1.61
3.14
0.43
6.42
0.93
0.09
1.03
4.93
1.90
0.21
f1 (ppm)

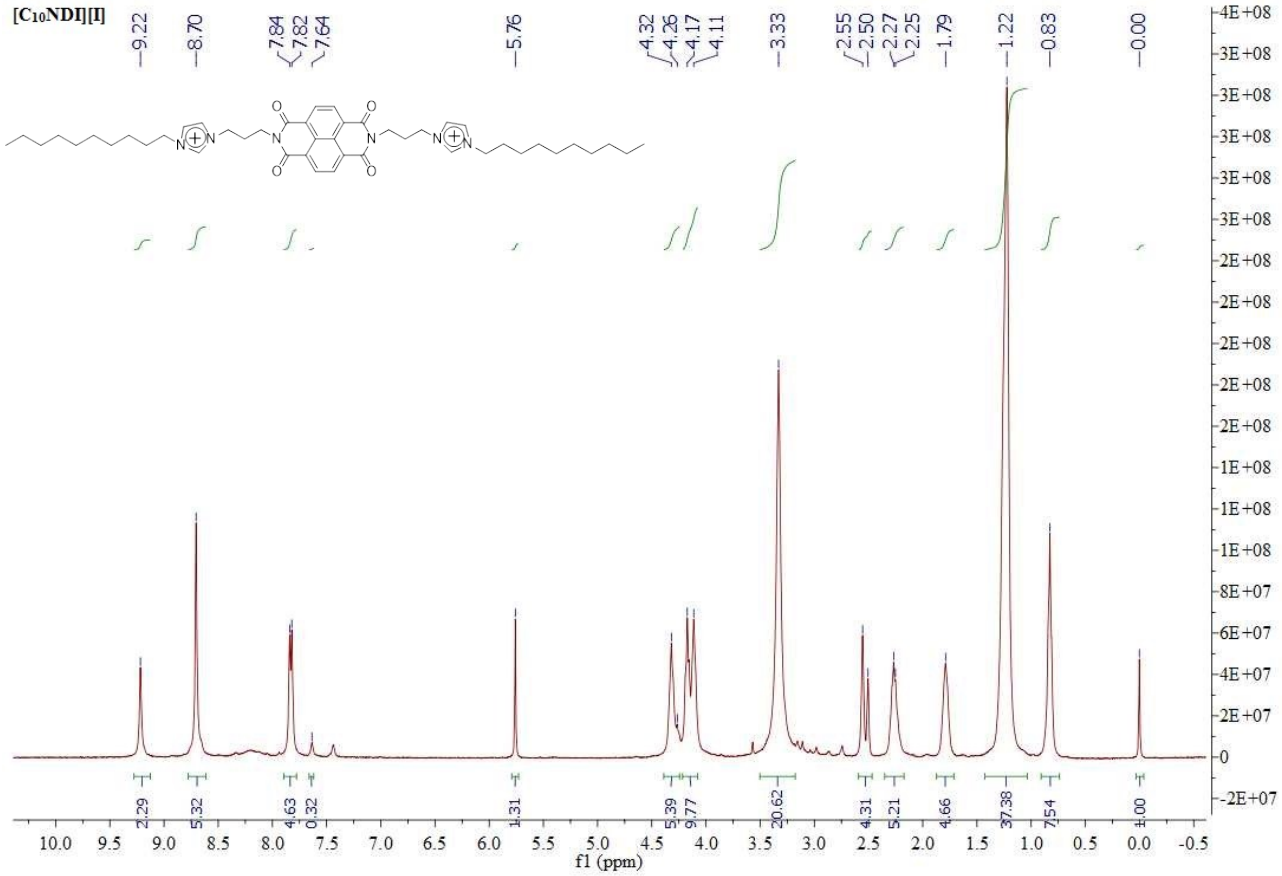

[C7NDI][I]
163.34
136.57
130.88
126.90
126.69
122.91
49.36
47.43
40.64
40.43
40.22
40.01
39.80
39.60
39.39
31.45
29.77
28.57
28.46
25.86
22.40
14.34
f1 (ppm)

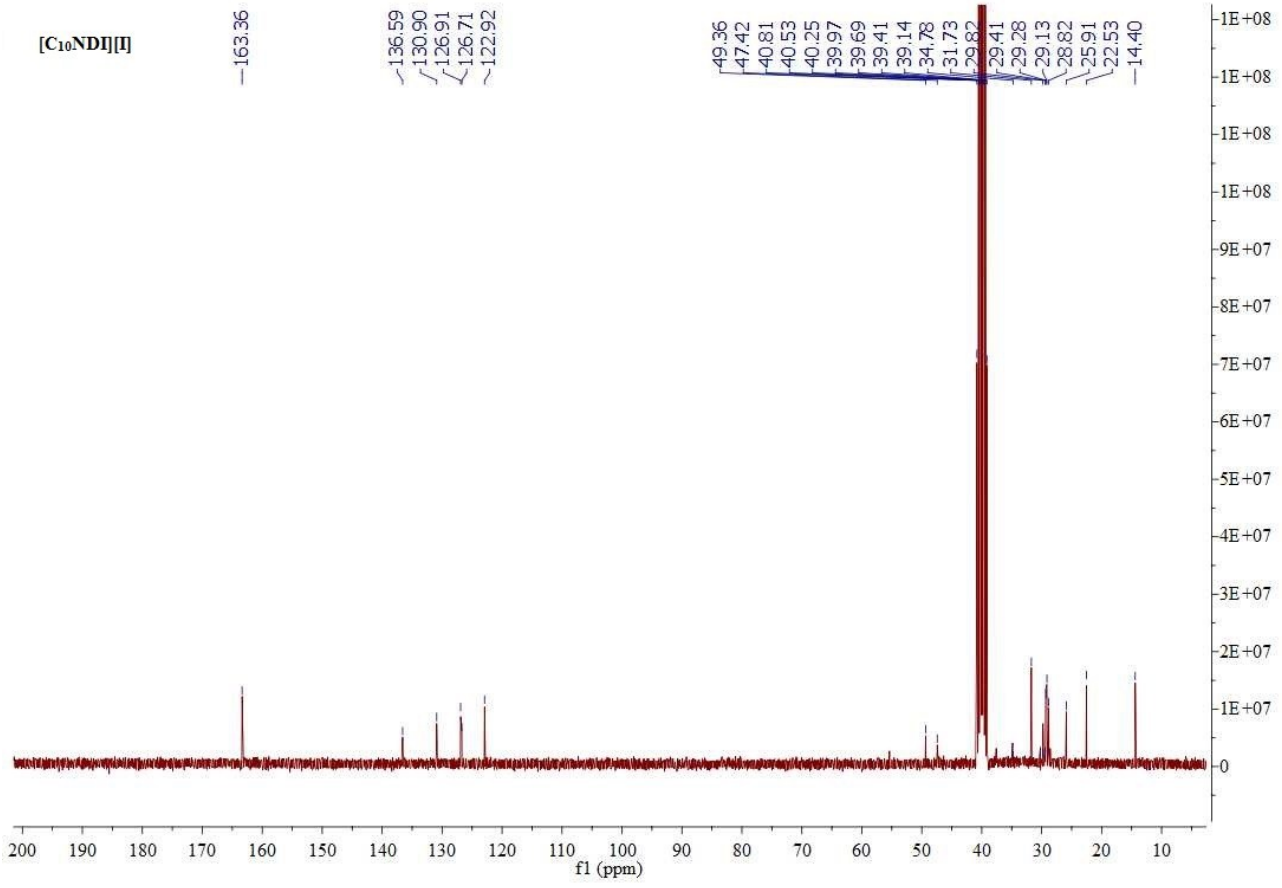

[C8NDI][I]
9.21
8.81
8.70
7.83
7.81
7.69
4.32
4.17
4.12
3.27
2.56
2.50
2.28
1.80
1.25
0.84
0.00
1.00
0.38
2.71
2.06
0.34
0.33
3.13
5.07
5.21
16.17
2.92
1.95
10.87
2.97
0.26
f1 (ppm)

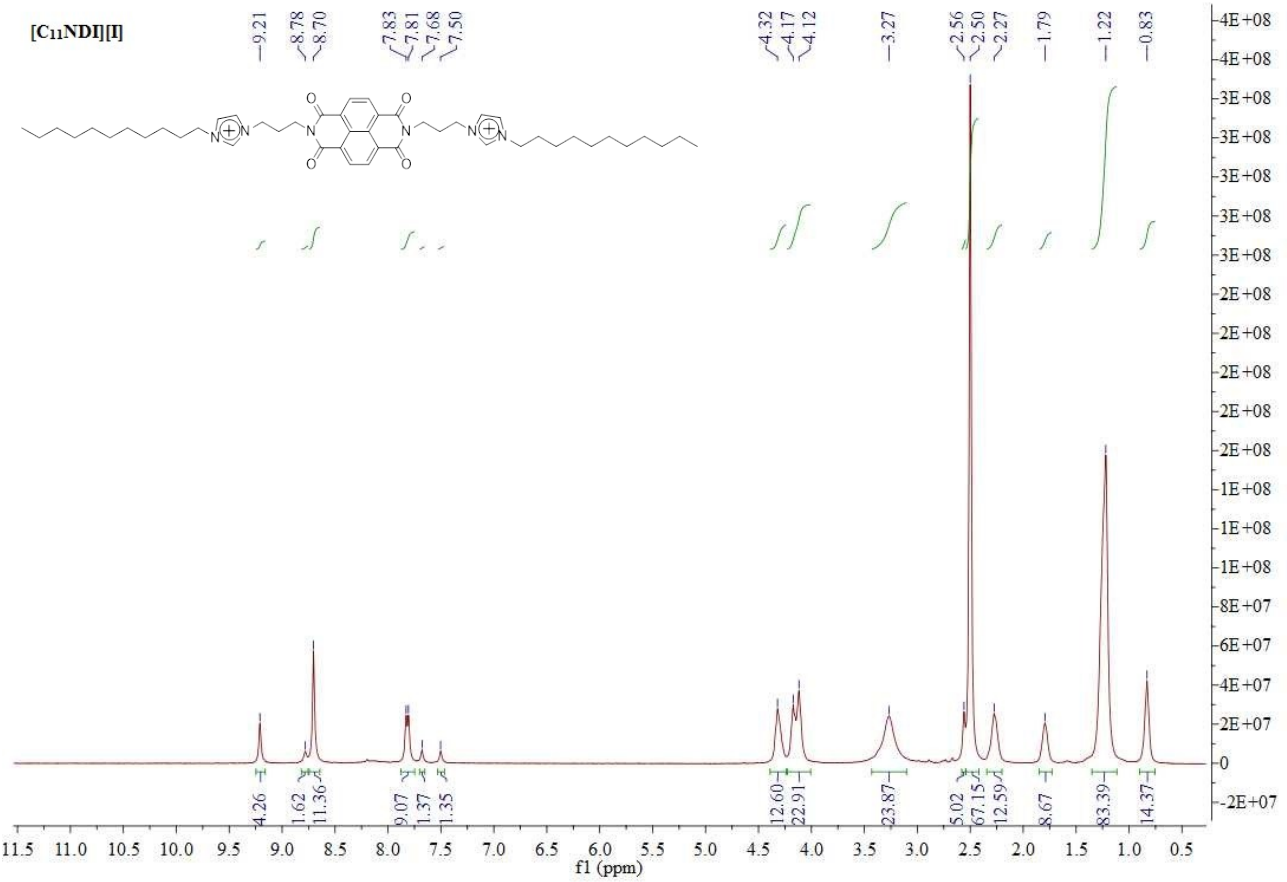

[C8NDI][I]
163.34
130.89
126.92
122.92
122.72
40.71
40.50
40.29
40.08
39.87
39.66
39.45
31.56
28.87
28.74
25.91
22.45
14.32
f1 (ppm)

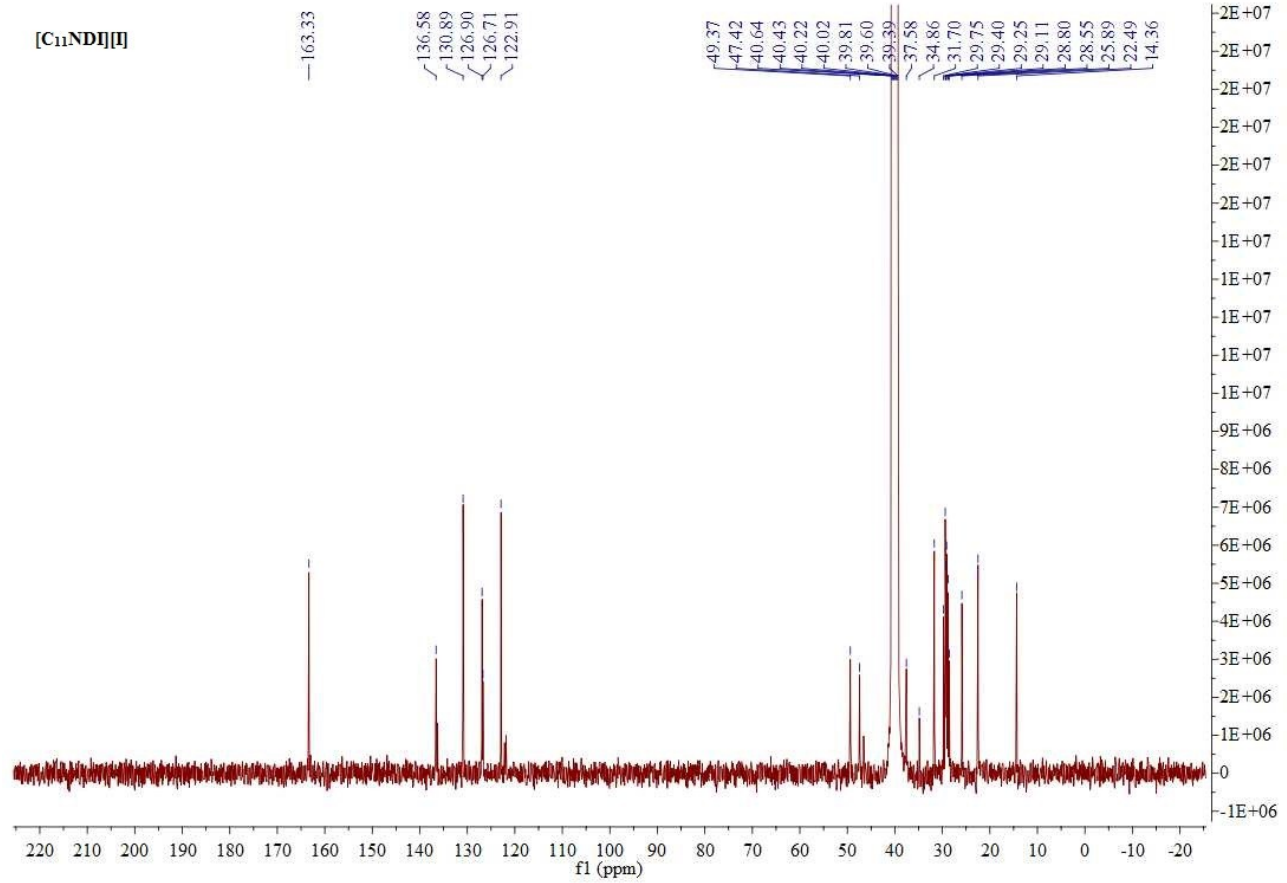

[C9NDI][I]
9.21
8.70
8.63
7.83
7.81
7.62
7.42
4.32
4.26
4.17
4.12
3.27
2.56
2.50
2.28
1.79
1.24
0.83
4.12
11.32
2.49
8.86
1.87
1.71
12.74
22.37
19.44
68.43
15.06
8.83
56.46
13.32
f1 (ppm)

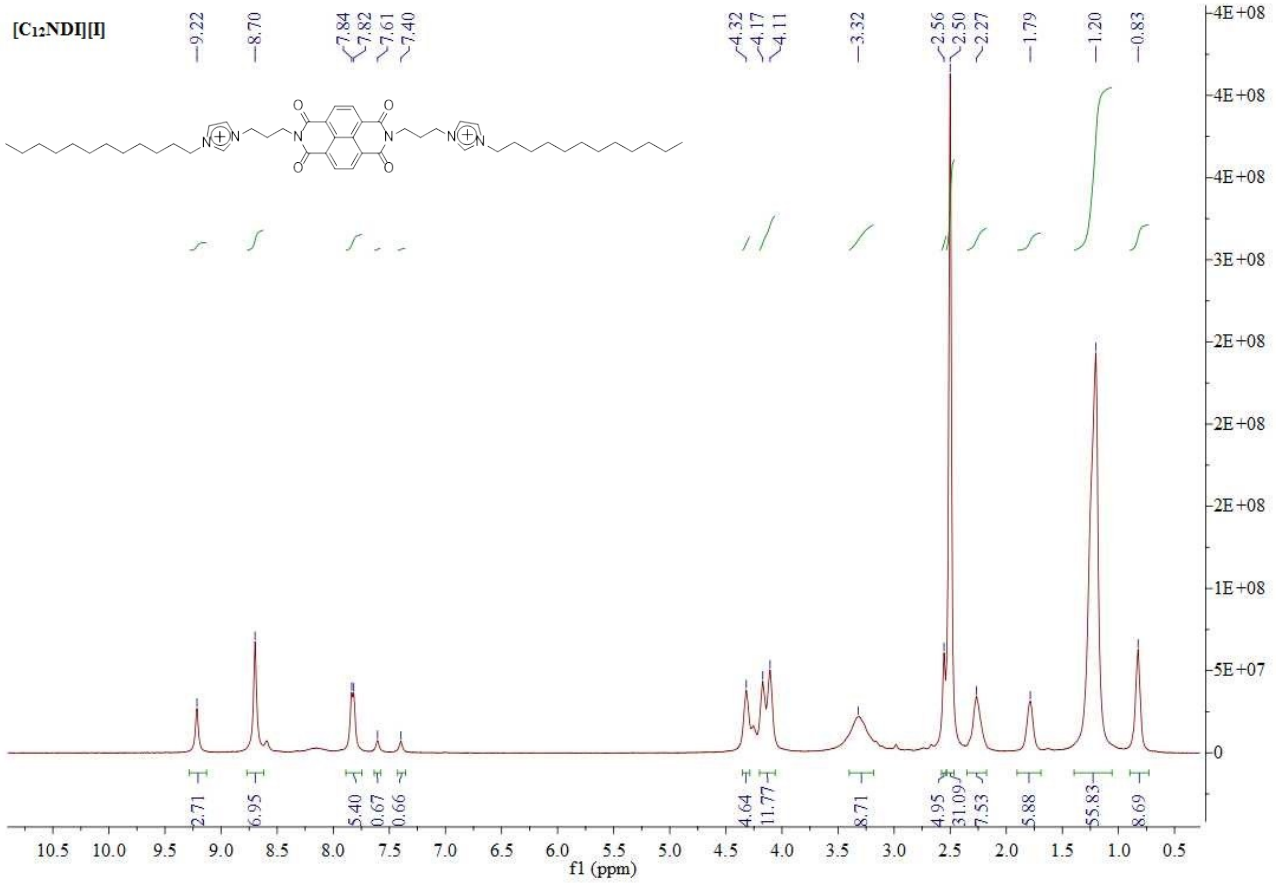

[C9NDI][I]
163.34
130.87
126.90
122.90
49.34
40.60
40.39
40.18
39.97
39.76
39.56
39.35
31.68
30.41
29.76
29.67
29.01
26.07
25.89
14.38
f1 (ppm)

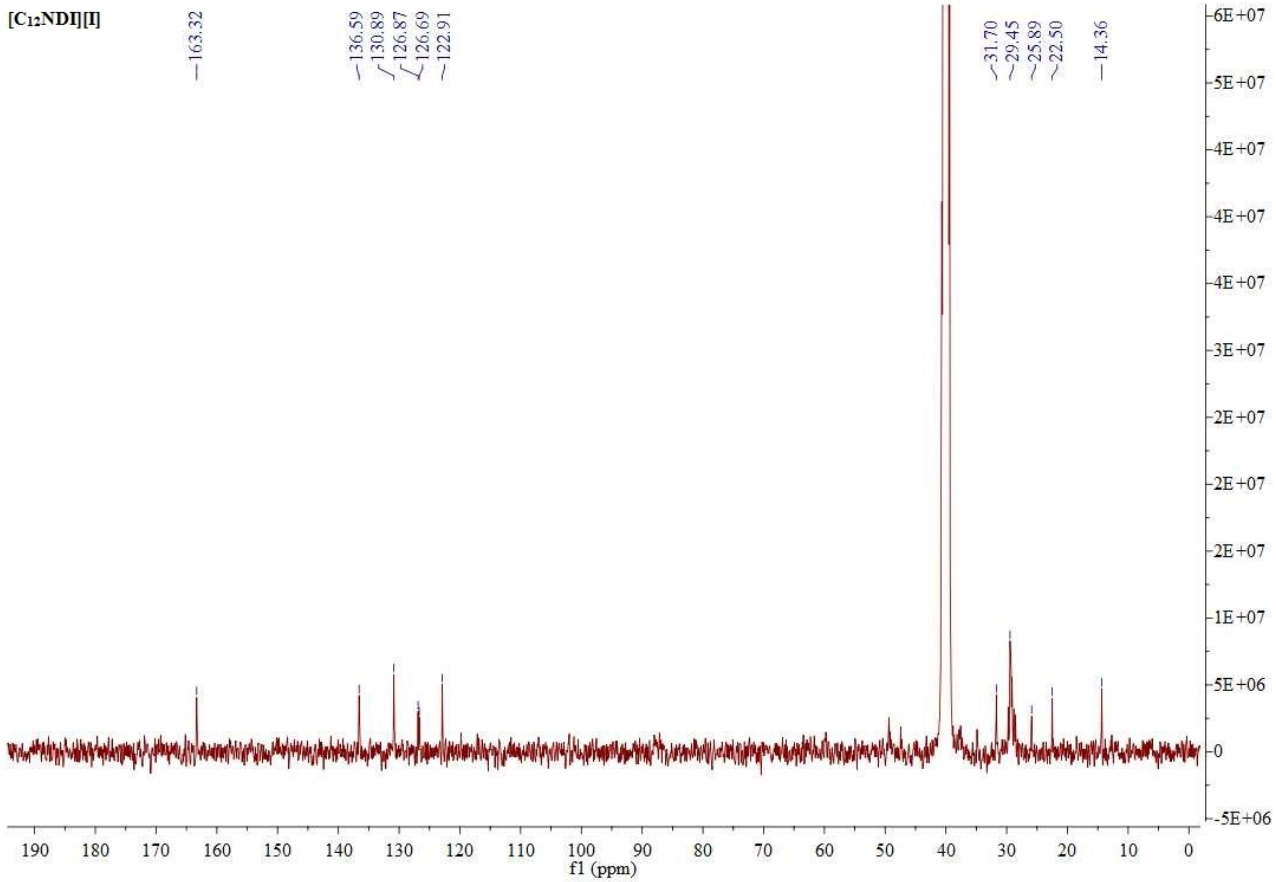

[C10NDI][I]
9.22
8.70
7.84
7.82
7.64
5.76
4.32
4.26
4.17
4.11
3.33
2.55
2.50
2.27
2.25
1.79
1.22
0.83
0.00
2.29
5.32
4.63
0.32
1.31
5.39
9.77
20.62
4.31
5.21
4.66
37.38
7.54
1.00
f1 (ppm)


[C10NDI][I]
163.36
136.59
130.90
126.91
126.71
122.92
49.36
47.42
40.81
40.53
40.25
39.97
39.69
39.41
39.14
34.78
31.73
29.82
29.41
29.28
29.13
28.82
25.91
22.53
14.40
f1 (ppm)


[C11NDI][I]
9.21
8.78
8.70
7.83
7.81
7.68
7.50
4.32
4.17
4.12
3.27
2.56
2.50
2.27
1.79
1.22
0.83
4.26
1.62
11.36
9.07
1.37
1.35
12.60
22.91
23.87
5.02
67.15
12.59
8.67
83.39
14.37
f1 (ppm)


[C11NDI][I]
163.33
136.58
130.89
126.90
126.71
122.91
49.37
47.42
40.64
40.43
40.22
40.02
39.81
39.60
39.39
37.58
34.86
31.70
29.75
29.40
29.25
29.11
28.80
28.55
25.89
22.49
14.36
f1 (ppm)


[C12NDI][I]
9.22
8.70
7.84
7.82
7.61
7.40
4.32
4.17
4.11
3.32
2.56
2.50
2.27
1.79
1.20
0.83
2.71
6.95
5.40
0.67
0.66
4.64
11.77
8.71
4.95
31.09
7.53
5.88
55.83
8.69
f1 (ppm)


[C12NDI][I]
163.32
136.59
130.89
126.87
126.69
122.91
31.70
29.45
25.89
22.50
14.36
f1 (ppm)

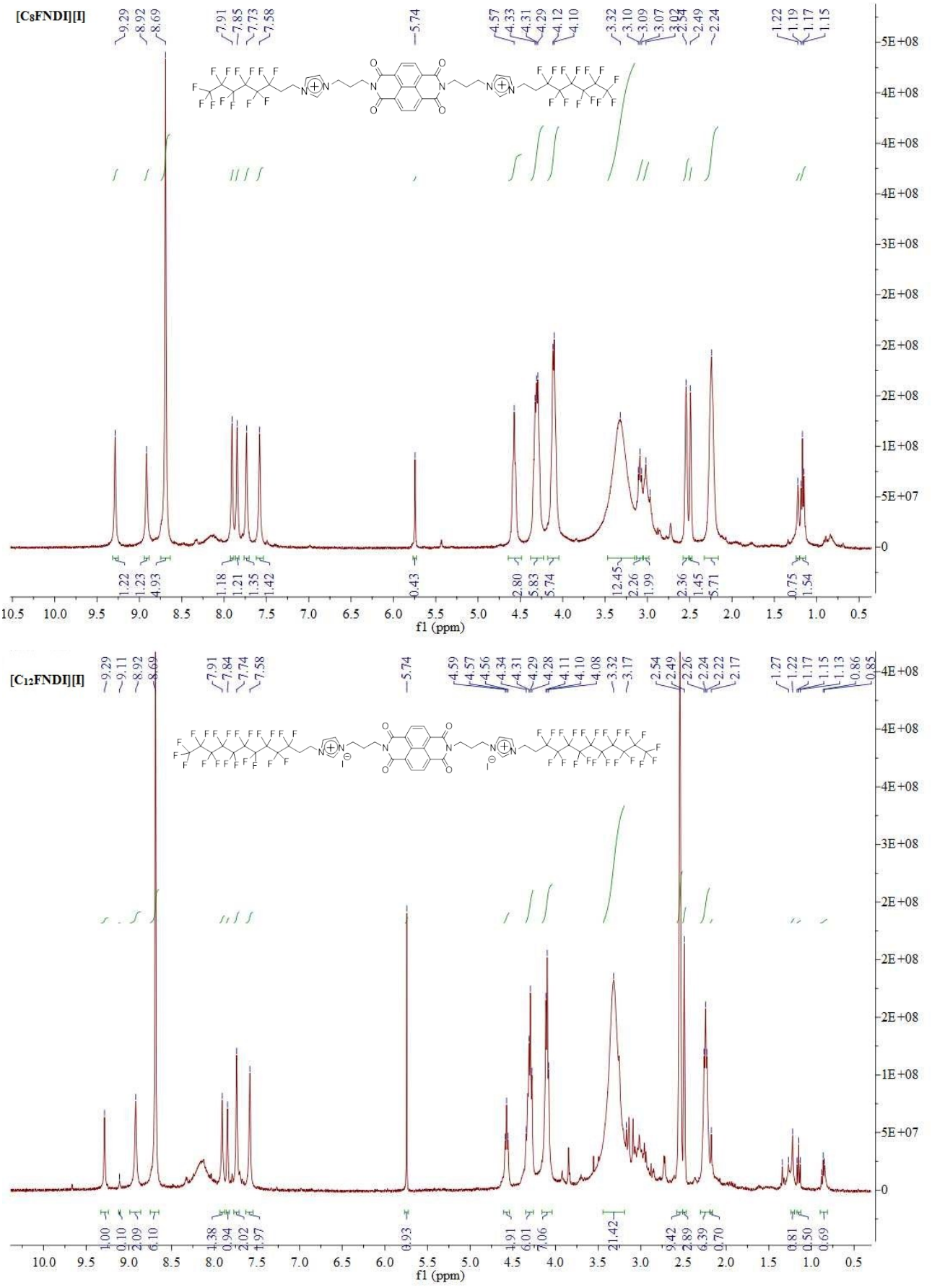
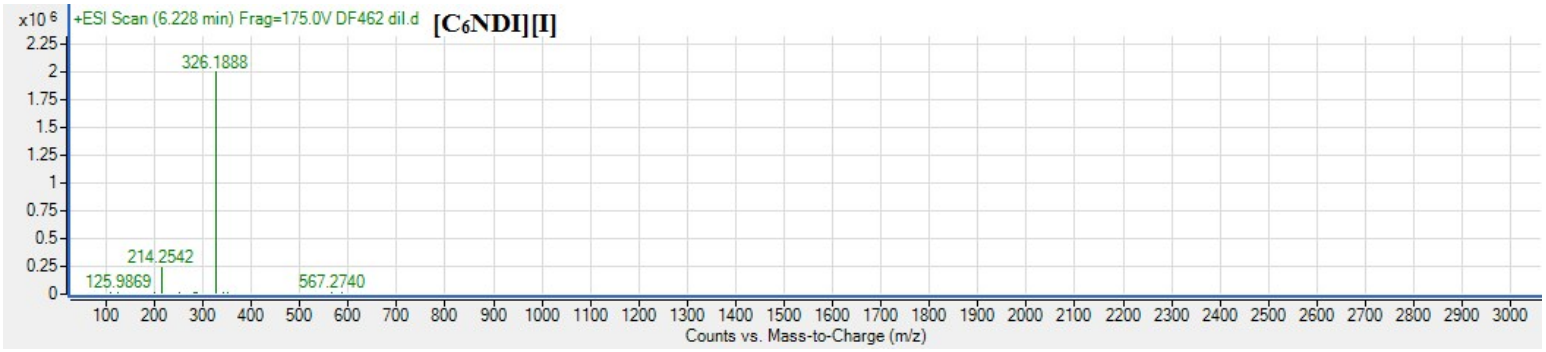
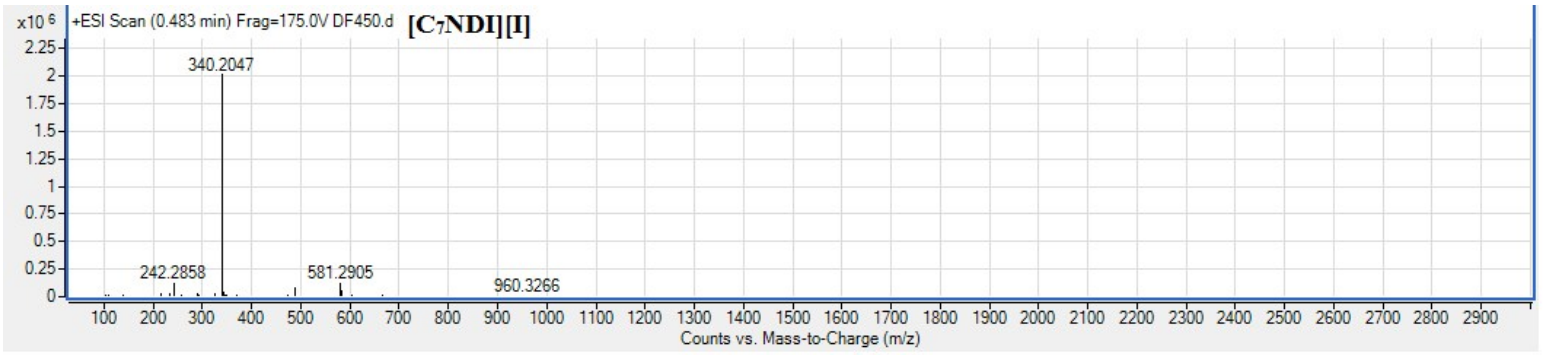
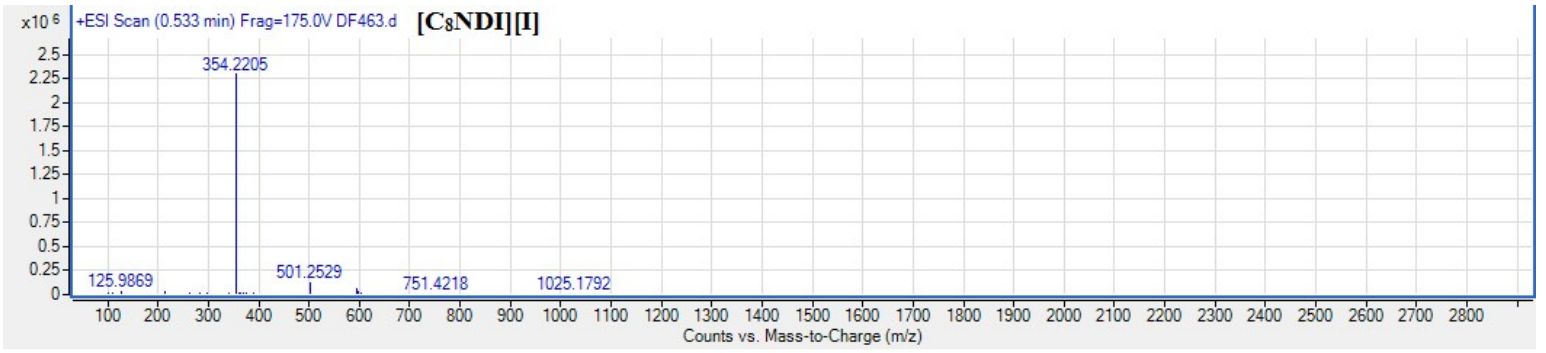
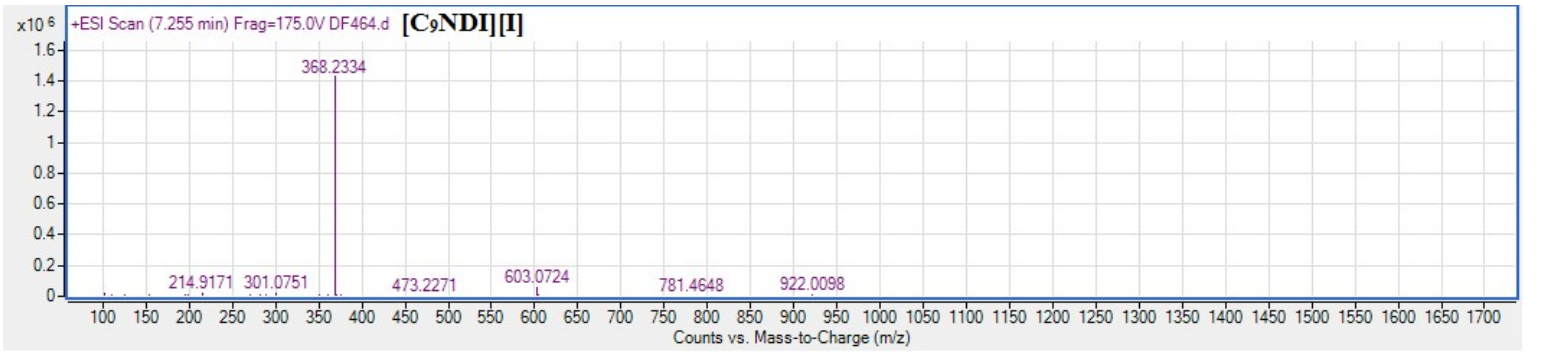


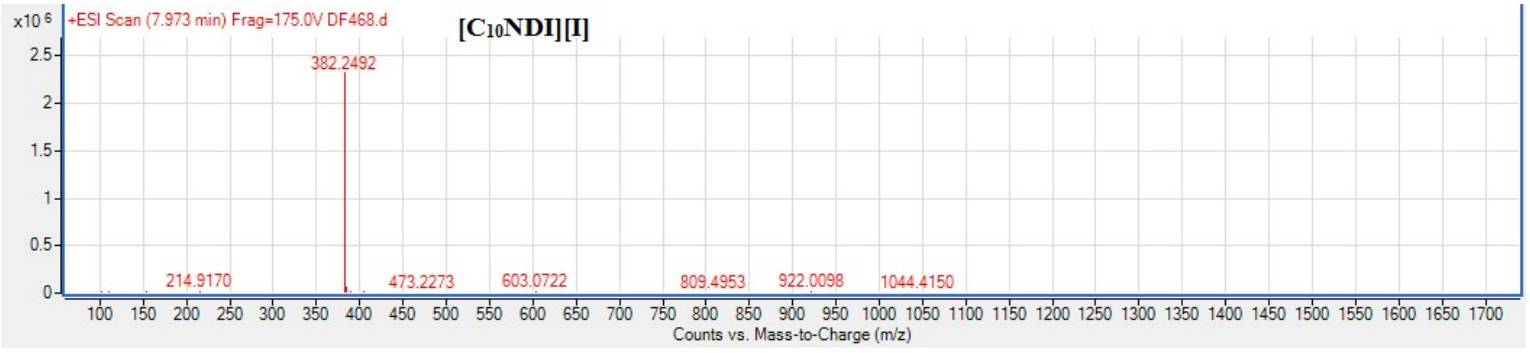
Figure S13. ^{1}HNMR and ^{13}C NMR spectra of synthesized salts.


x10 6
+ESI Scan (6.228 min) Frag=175.0V DF462 dil.d
[C6NDI][I]
326.1888
214.2542
125.9869
567.2740
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (0.483 min) Frag=175.0V DF450.d
[C7NDI][I]
340.2047
242.2858
581.2905
960.3266
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (0.533 min) Frag=175.0V DF463.d
[C8NDI][I]
354.2205
125.9869
501.2529
751.4218
1025.1792
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (7.255 min) Frag=175.0V DF464.d
[C9NDI][I]
368.2334
214.9171
301.0751
473.2271
603.0724
781.4648
922.0098
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (7.973 min) Frag=175.0V DF468.d
[C10NDI][I]
382.2492
214.9170
473.2273
603.0722
809.4953
922.0098
1044.4150
Counts vs. Mass-to-Charge (m/z)

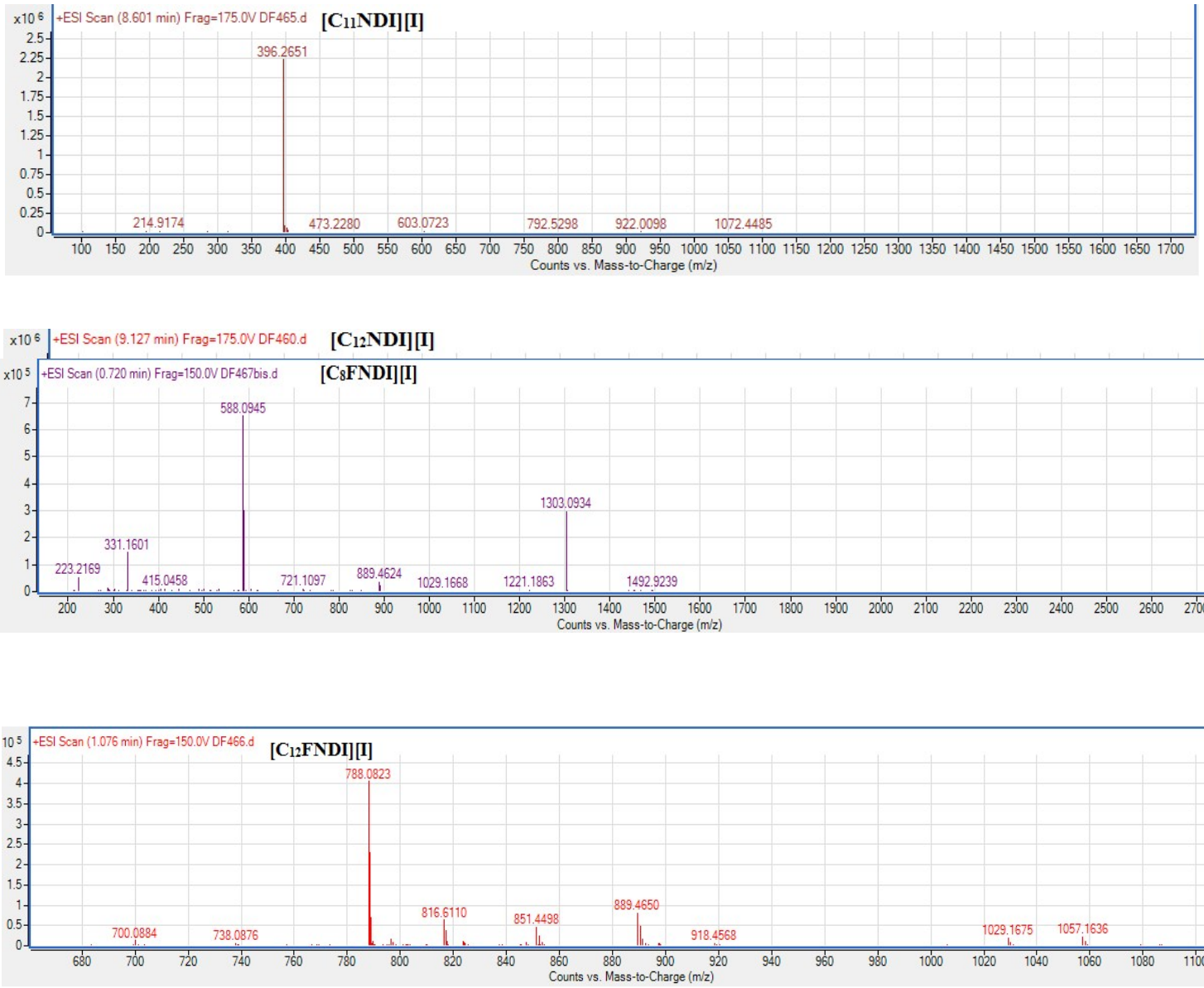


Figure S14.ESI Mass spectra of synthesized salts.