Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

π-conjugated diimidazolium salts: rigid structures to obtain organized materials

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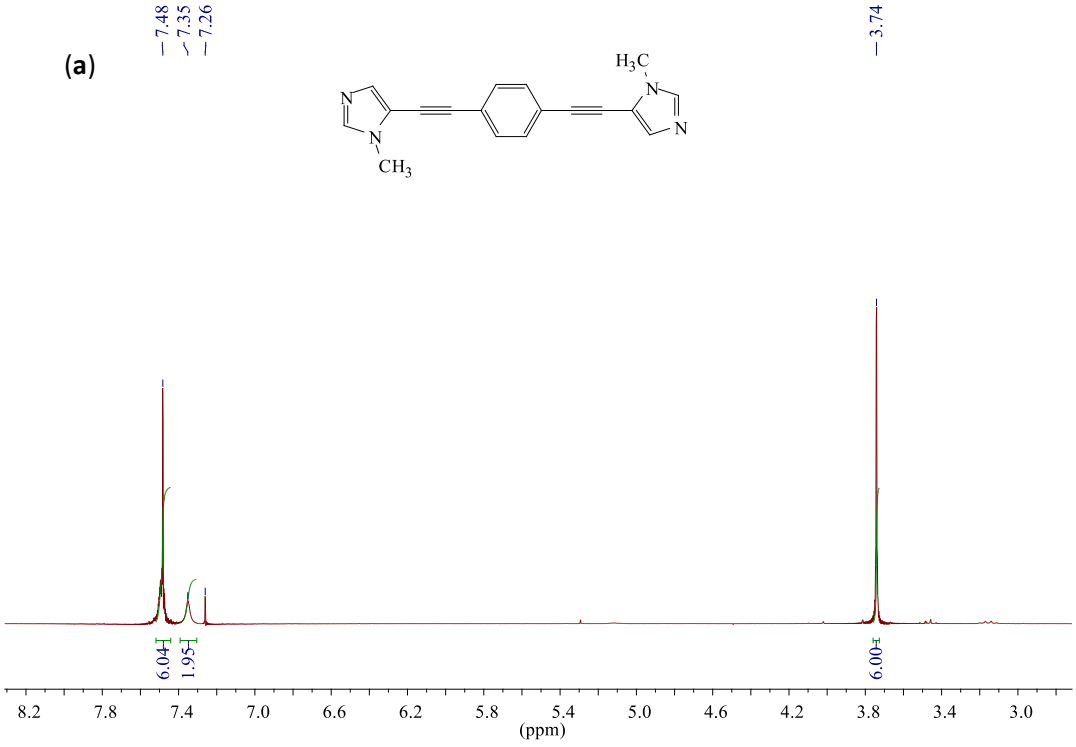
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3.4
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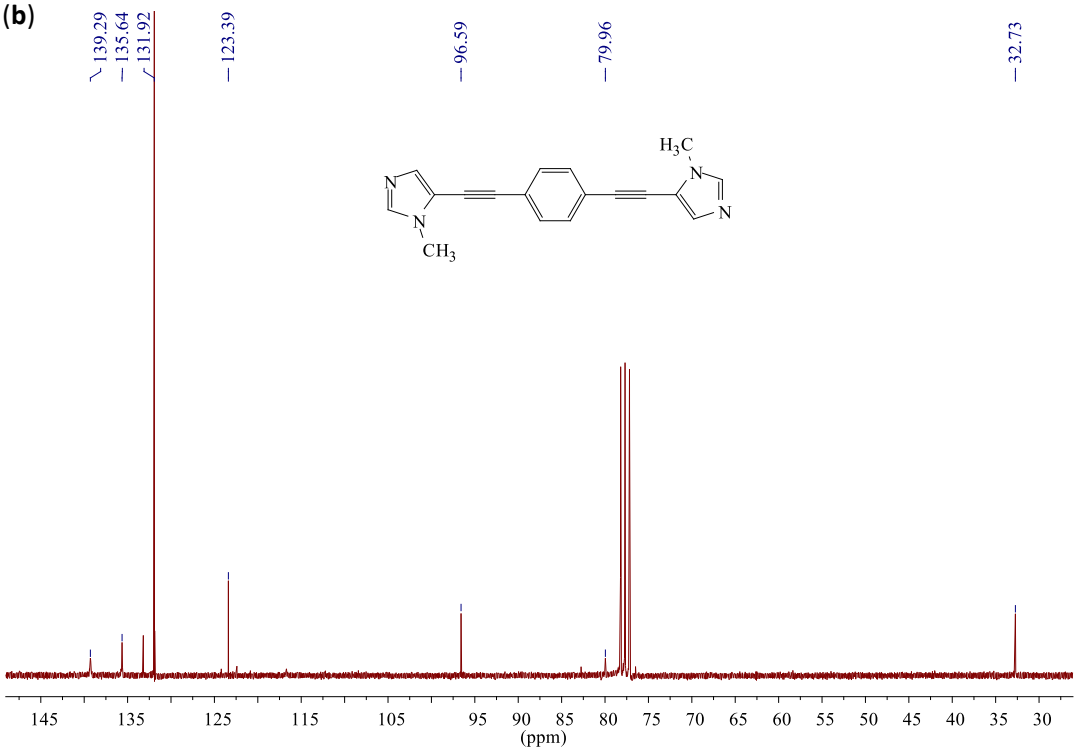
(b)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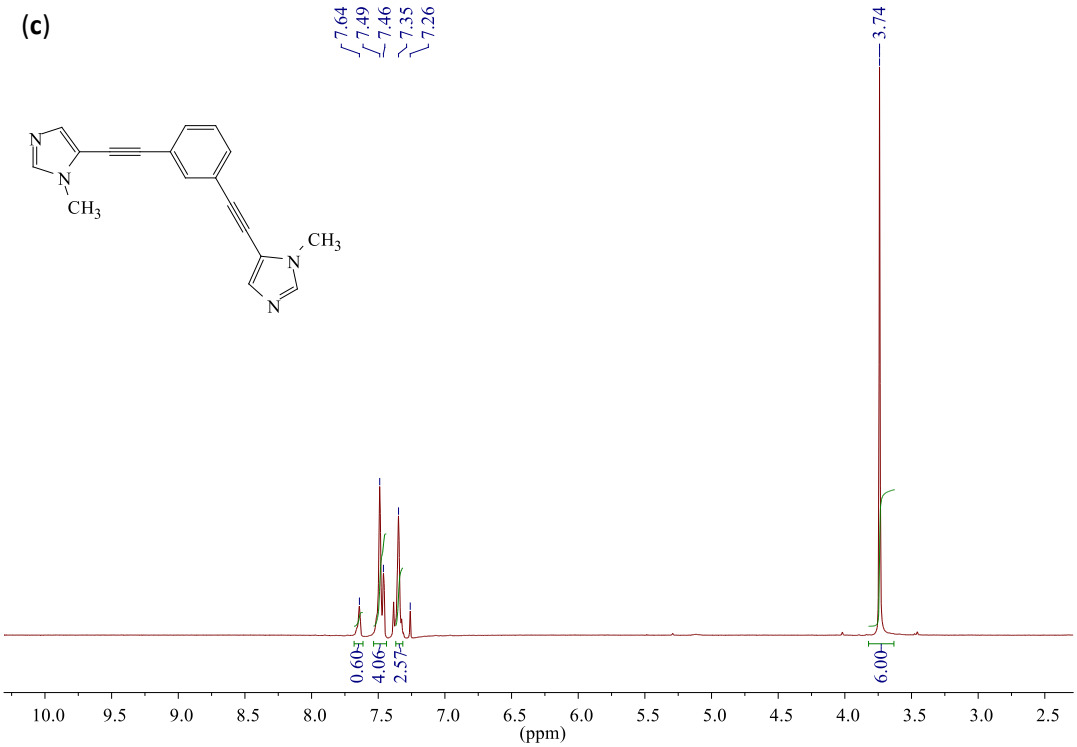
(ppm)

(c)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2.57
6.00
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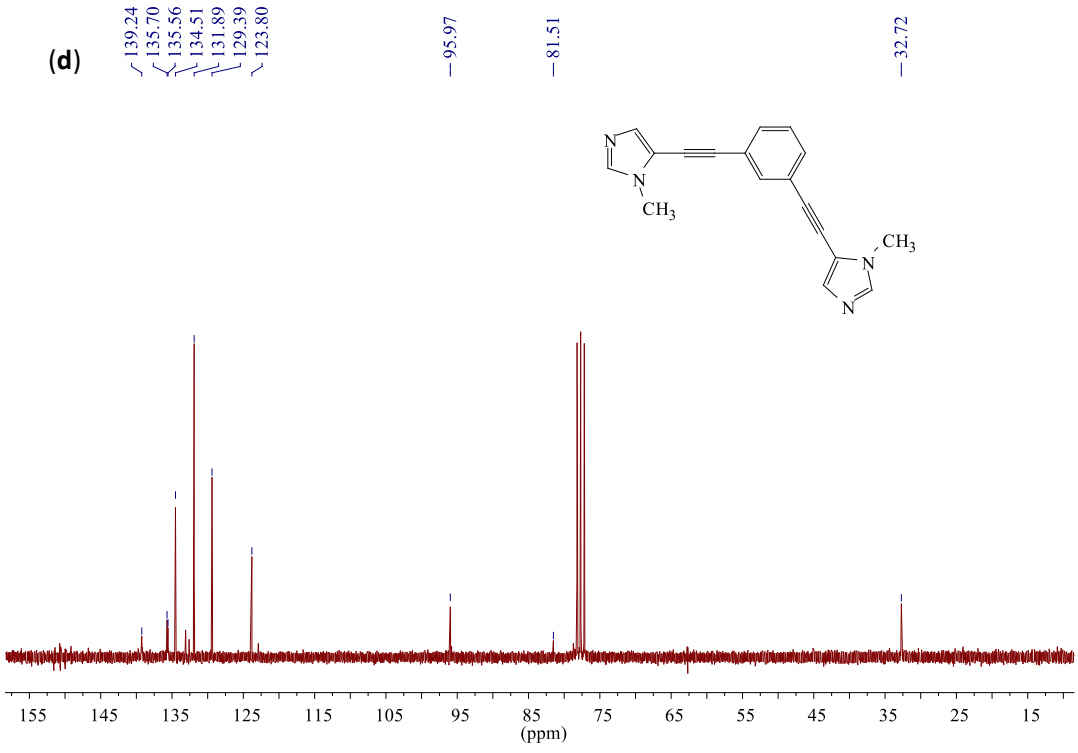
(ppm)

(d)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32.72
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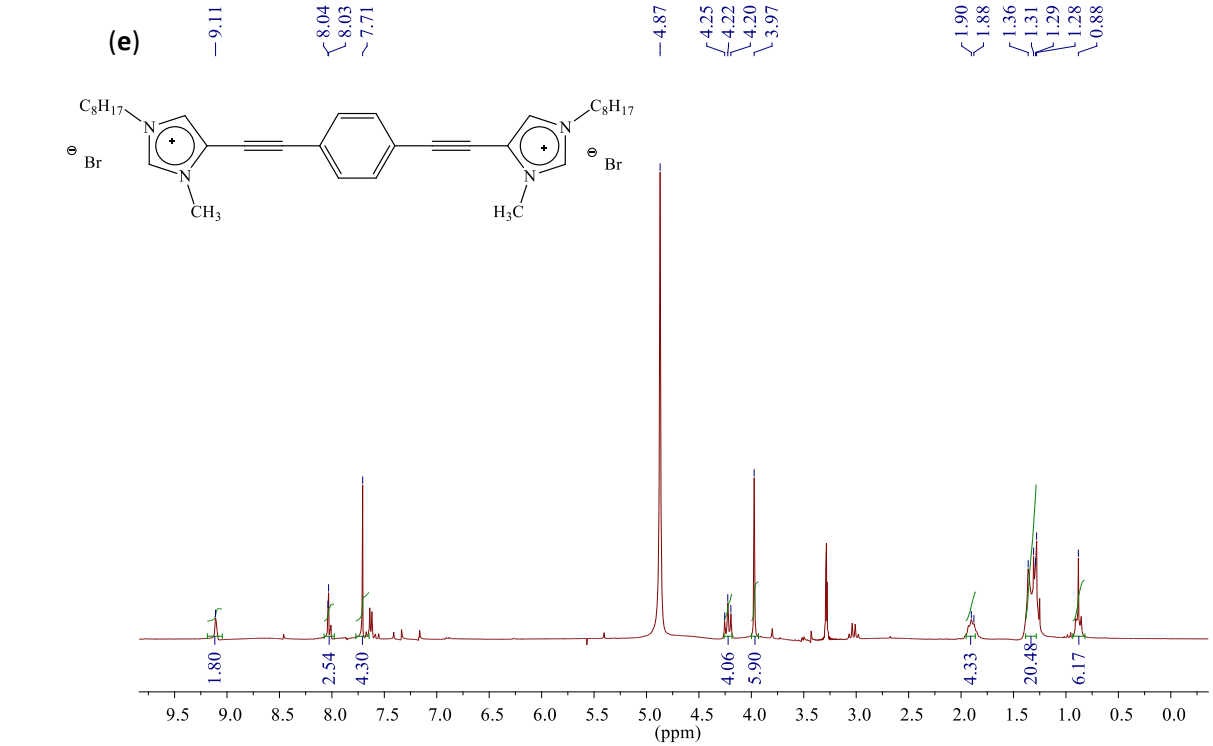
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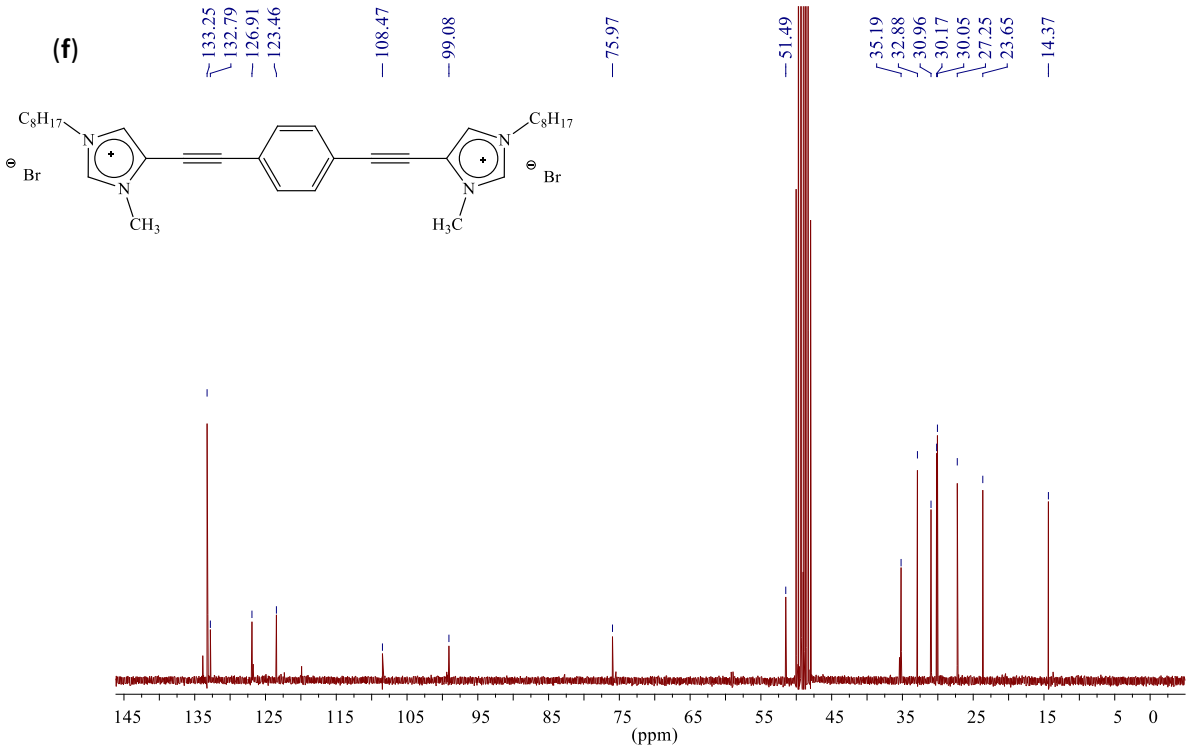
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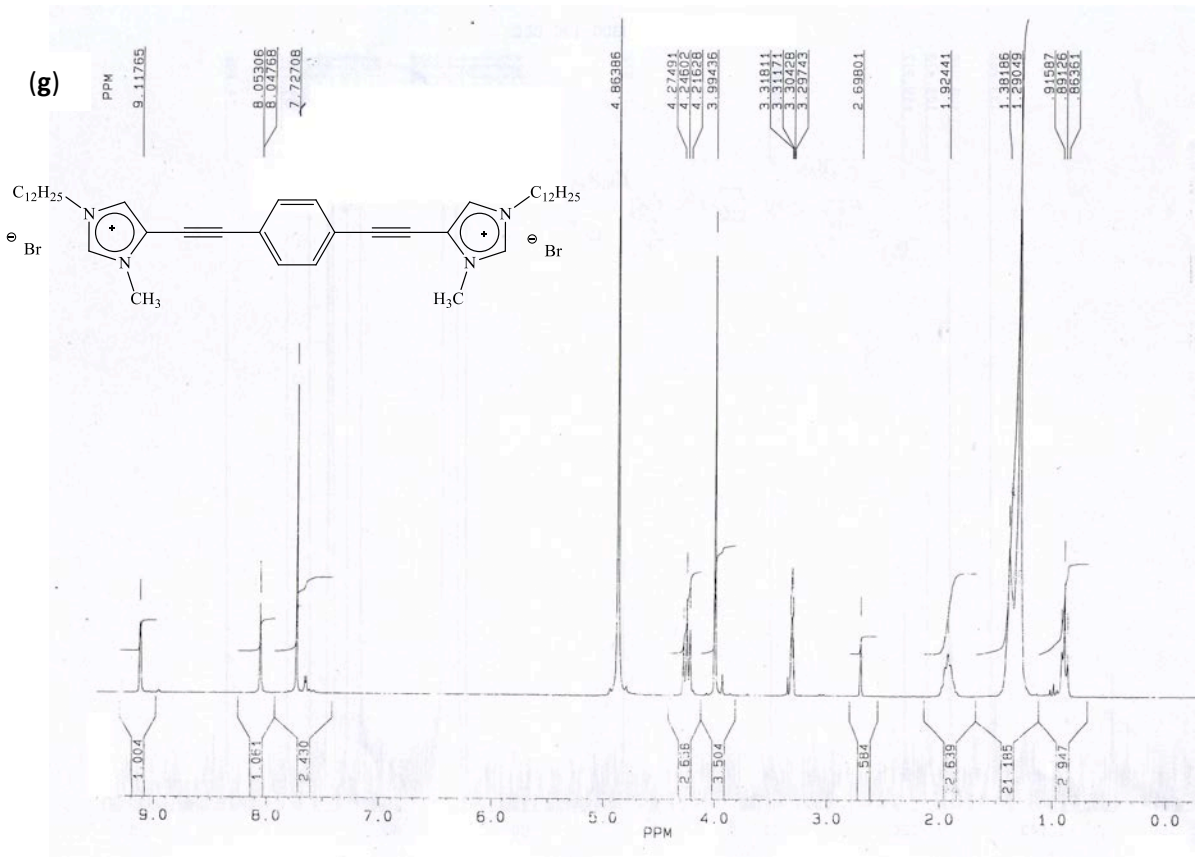
14.37
(ppm)

(g)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3.30428
3.29743
2.69801
1.92441
1.38186
1.29049
.91587
.89126
.86361
1.004
1.061
2.430
2.636
3.504
.584
2.639
21.185
2.947
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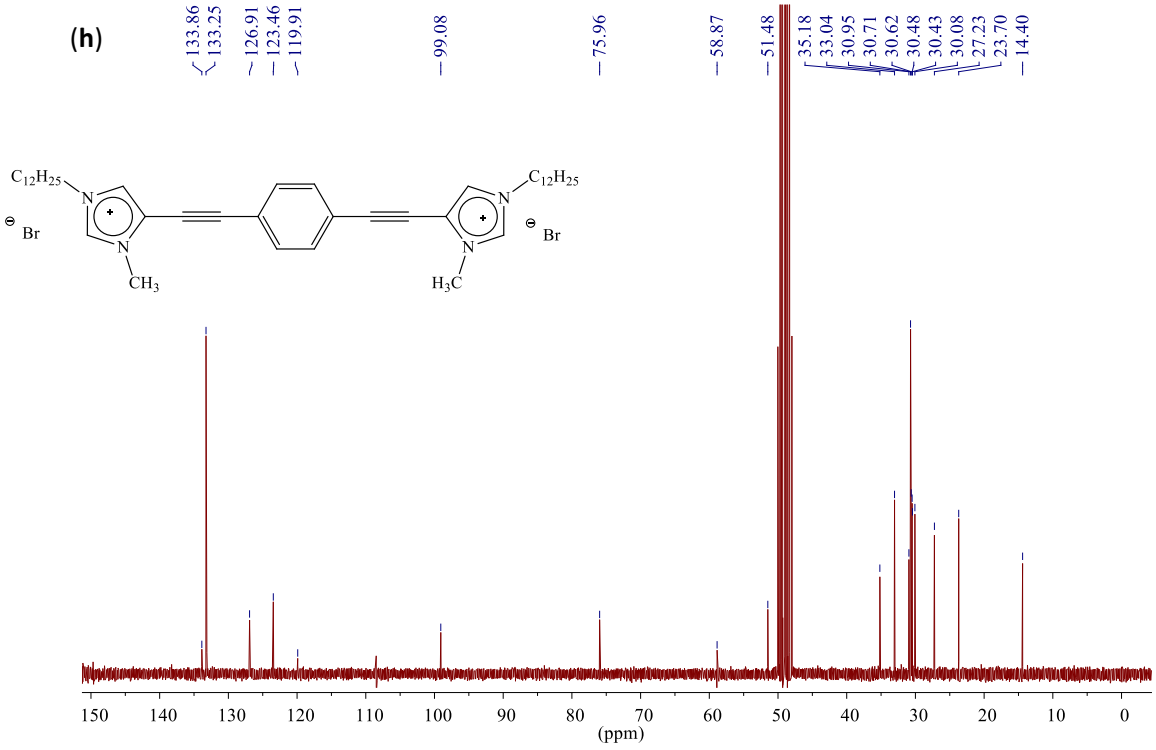
2.0
1.0
0.0
PPM

(h)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30.48
30.43
30.08
27.23
23.70
14.40
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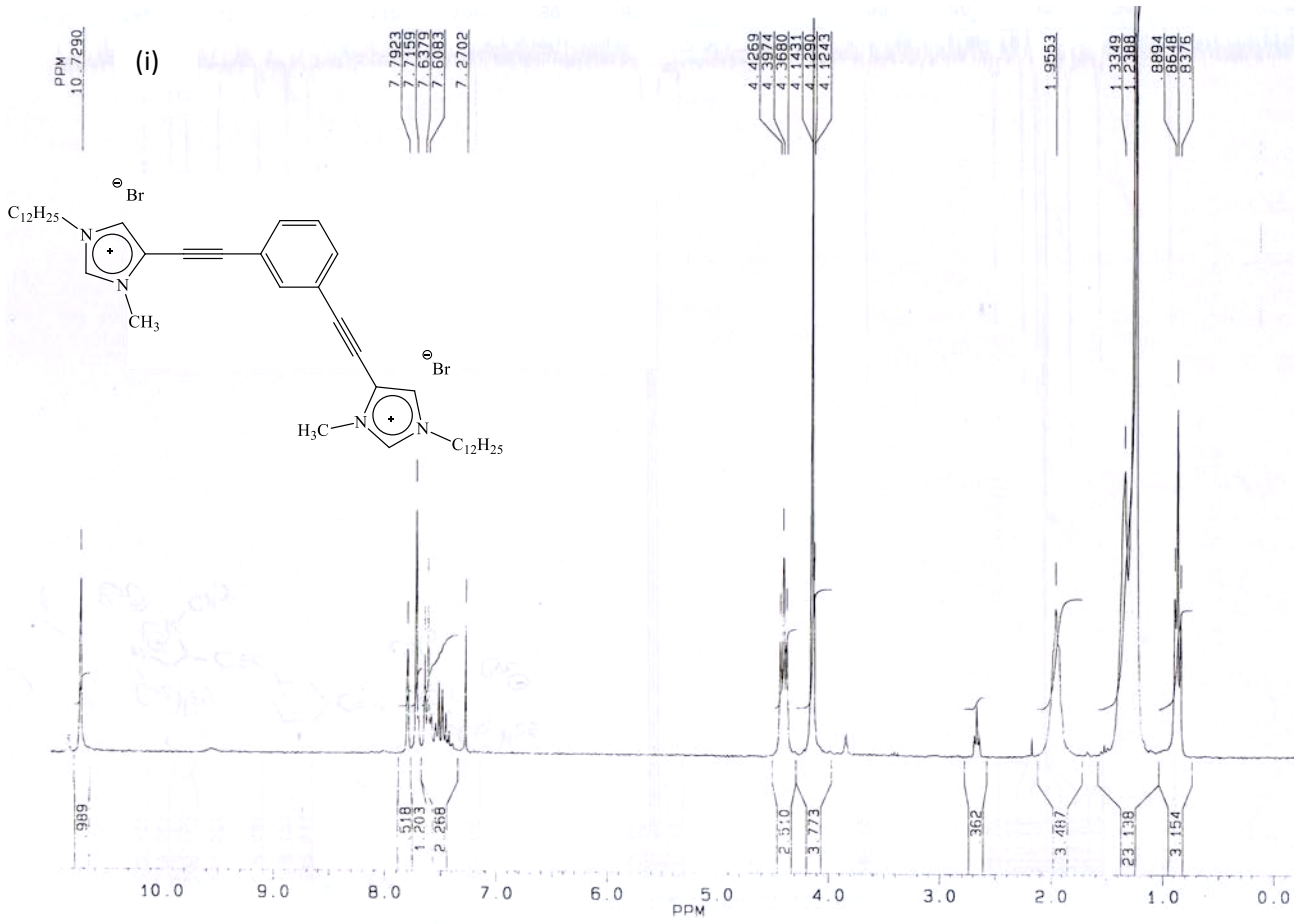
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

(i)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7.6083
7.2702
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4.1431
4.1290
4.1243
1.9553
1.3349
1.2388
.8894
.8648
.8376
Br
$C_{12}H_{25}$
N
N
CH_3
Br
H_3C
N
N
$C_{12}H_{25}$
.989
.518
1.203
2.268
2.510
3.773
.362
3.487
23.138
3.154
10.0
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7.0
6.0
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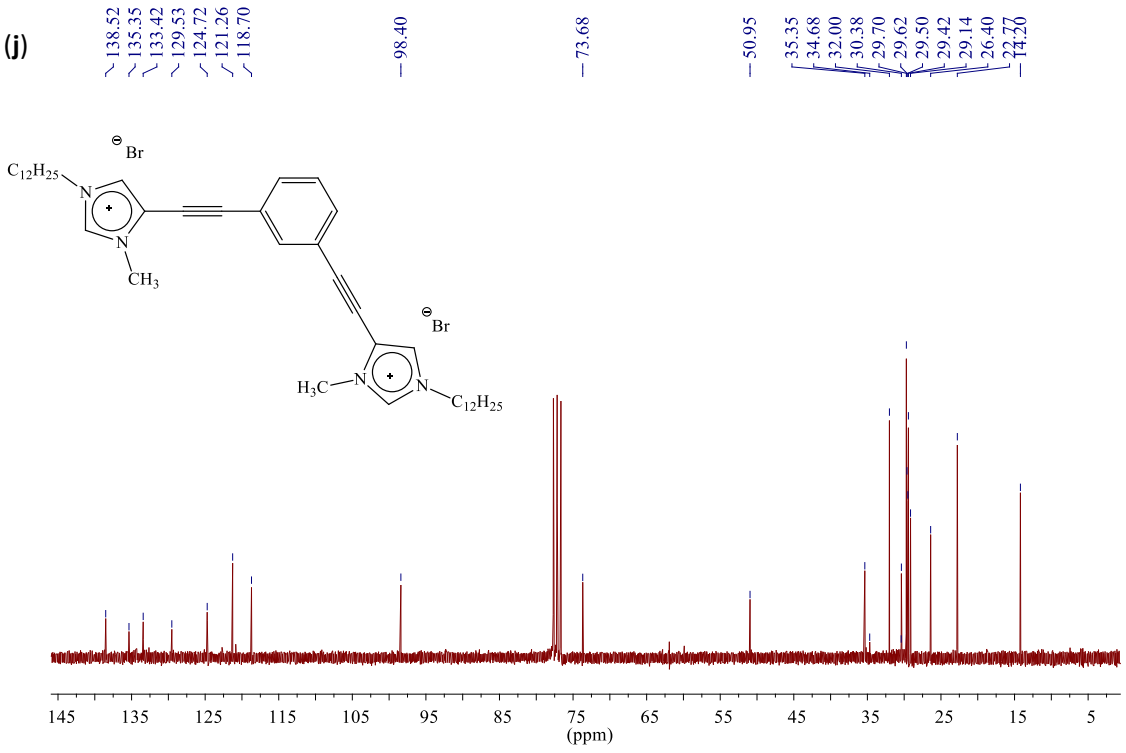
1.0
0.0
ppm

(j)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32.00
30.38
29.70
29.62
29.50
29.42
29.14
26.40
22.77
14.20
Br
$C_{12}H_{25}$
N
N
CH_3
Br
H_3C
N
N
$C_{12}H_{25}$
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105
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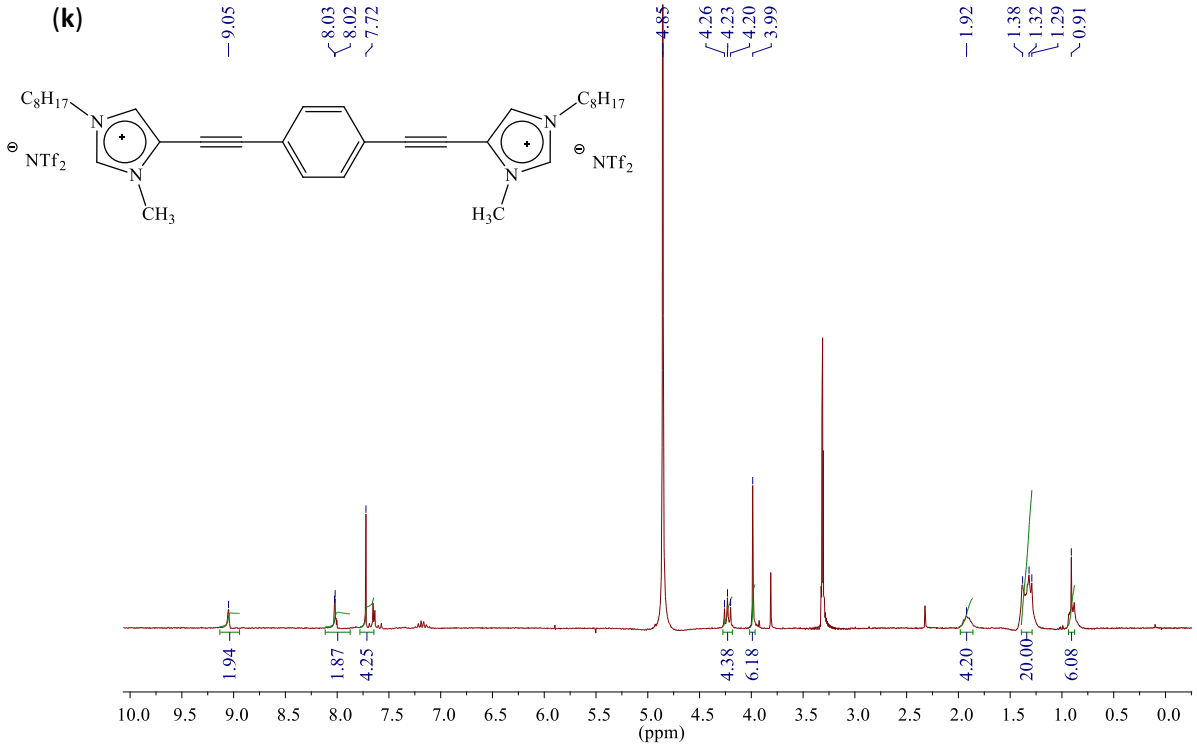
5
(ppm)

(k)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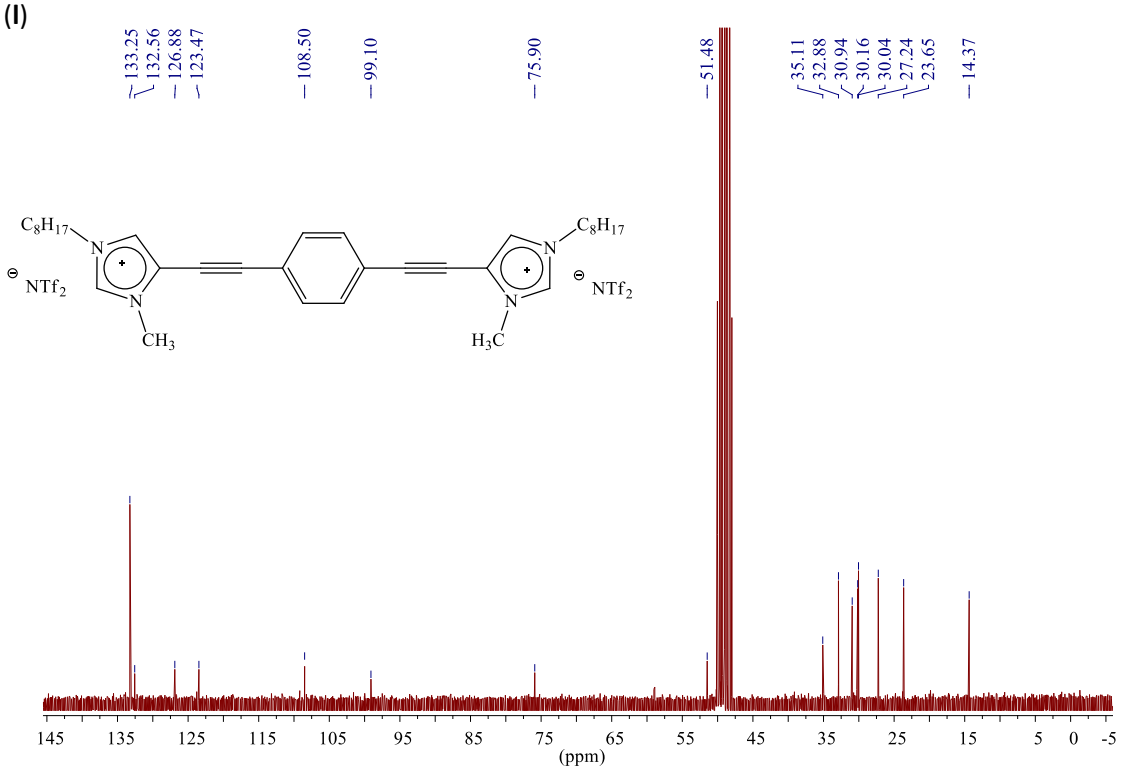
8.02
7.72
4.85
4.26
4.23
4.20
3.99
1.92
1.38
1.32
1.29
0.91
C_8H_{17}
N
$\ominus$ NTf_2
CH_3
H_3C
1.94
1.87
4.25
4.38
6.18
4.20
20.00
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

(l)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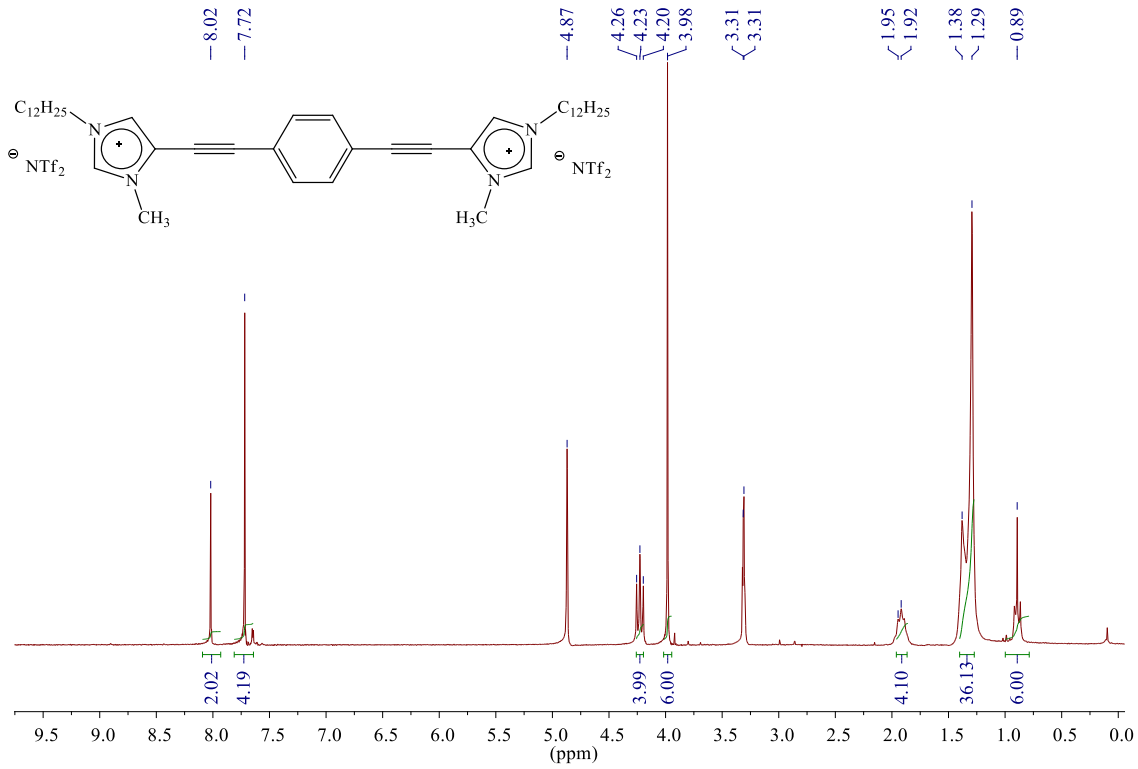
108.50
99.10
75.90
51.48
35.11
32.88
30.94
30.16
30.04
27.24
23.65
14.37
C_8H_{17}
N
$\ominus$ NTf_2
CH_3
H_3C
145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 0 -5
(ppm)

(m)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1.95
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4.19
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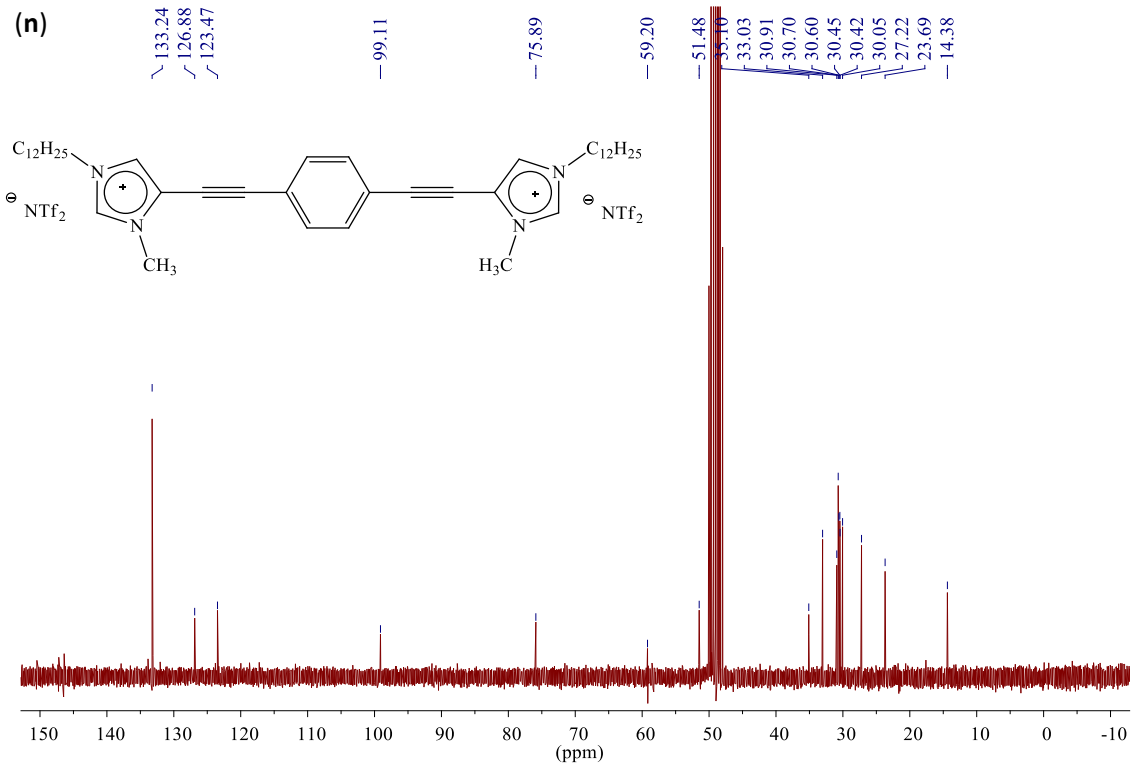
6.00
4.10
36.13
6.00
(ppm)

(n)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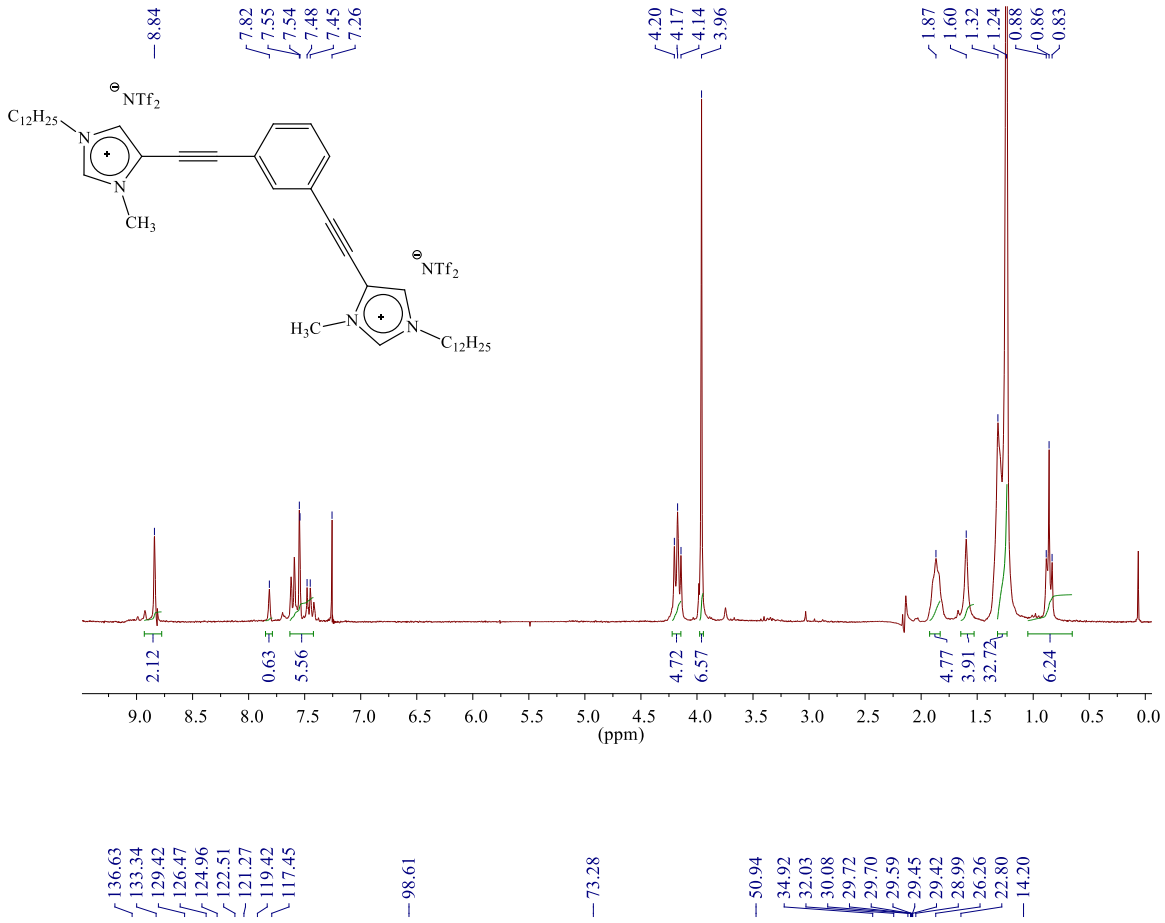
23.69
14.38
(ppm)

(o)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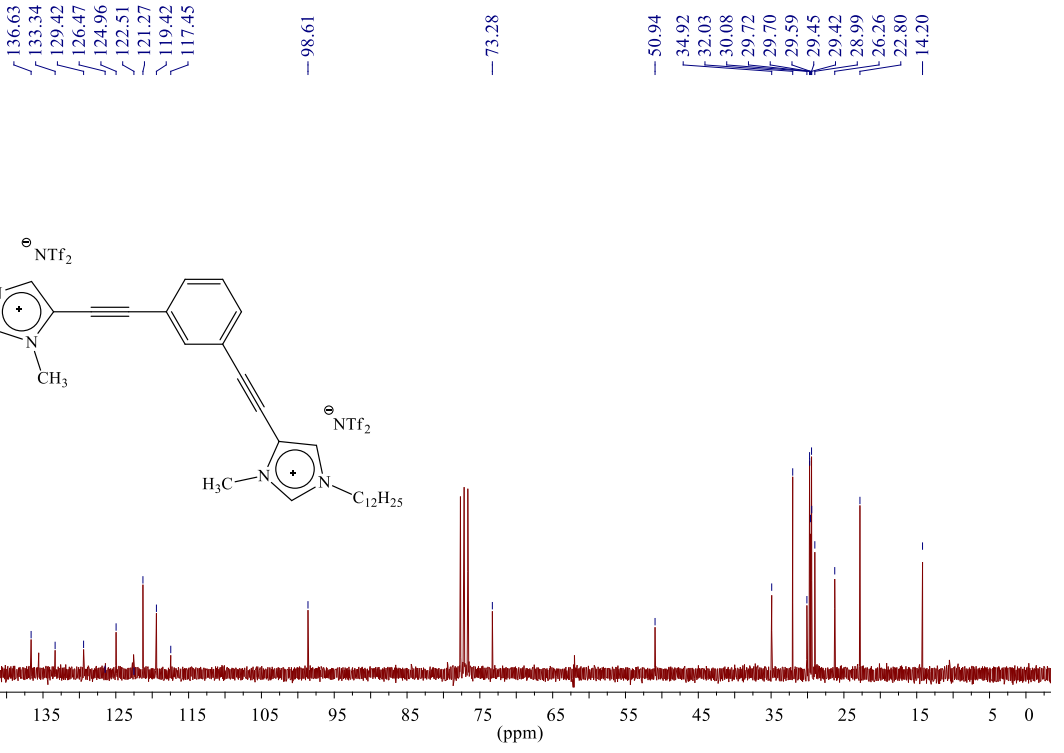
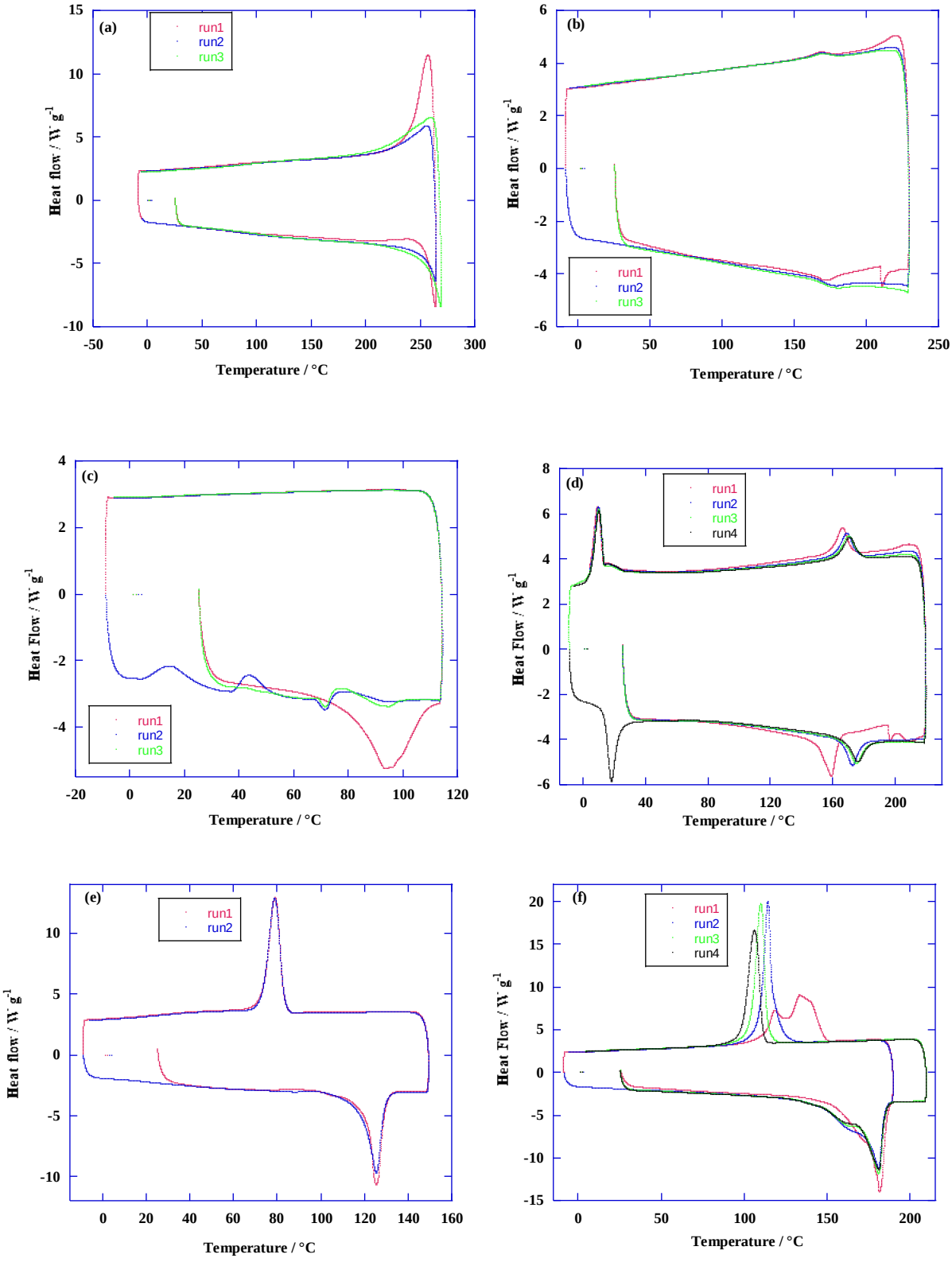
7.55
7.54
7.48
7.45
7.26
4.20
4.17
4.14
3.96
1.87
1.60
1.32
1.24
0.88
0.86
0.83
NTf2
C12H25
N
N
CH3
H3C
2.12
0.63
5.56
4.72
6.57
4.77
3.91
32.72
6.24
(ppm)


136.63
133.34
129.42
126.47
124.96
122.51
121.27
119.42
117.45
98.61
73.28
50.94
34.92
32.03
30.08
29.72
29.70
29.59
29.45
29.42
28.99
26.26
22.80
14.20
NTf2
C12H25
N
N
CH3
H3C
(ppm)

(p)

Fig. S1 ^{1}H NMR and ^{13}C NMR spectra corresponding to: (**a**), (**b**) **1**; (**c**), (**d**) **2**; (**e**), (**f**) [*p*-C_8Br_2]; (**g**), (**h**) [*p*-$C_{12}Br_2$]; (**i**), (**j**) [*m*-$C_{12}Br_2$]; (**k**), (**l**) [*p*-$C_8(NTf_2)_2$]; (**m**), (**n**) [*p*-$C_{12}(NTf_2)_2$] and (**o**), (**p**) [*m*-$C_{12}(NTf_2)_2$].



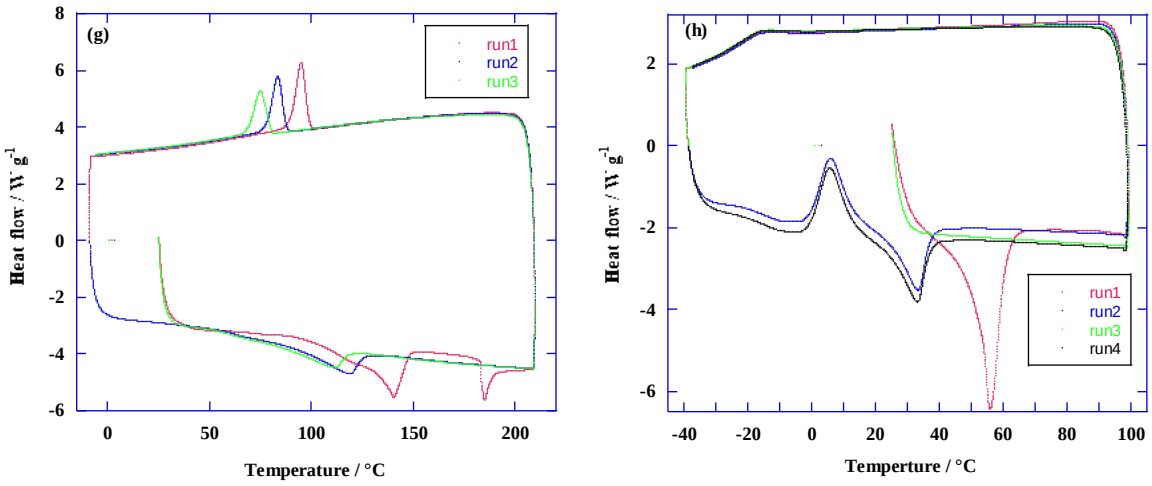
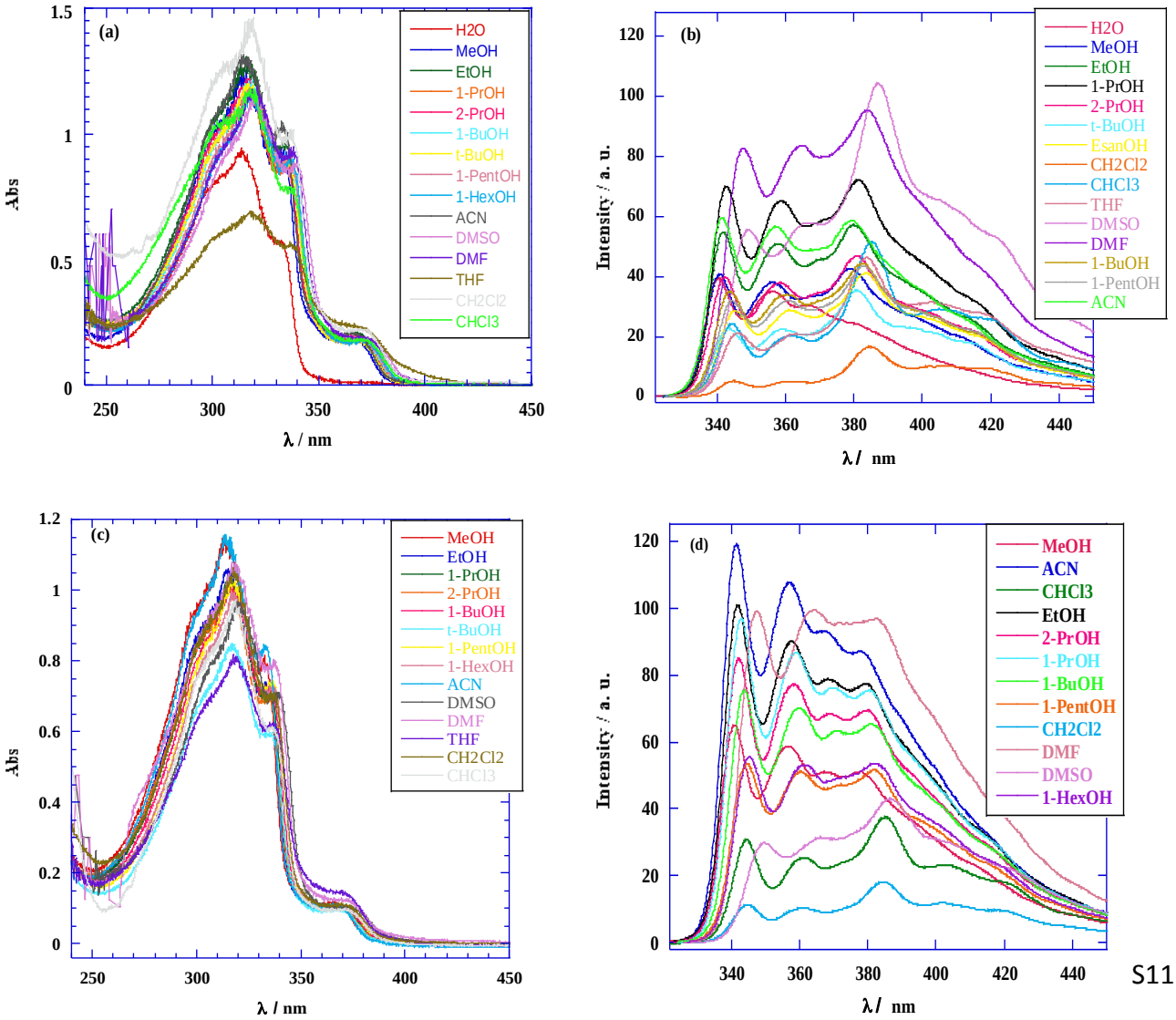


Fig. S2 DSC traces corresponding to: (**a**) **1**; (**b**) [*p*-C_8Br_2]; (**c**) [*p*-$C_8(NTf_2)_2$]; (**d**) [*p*-$C_{12}Br_2$]; (**e**) [*p*-$C_{12}(NTf_2)_2$]; (**f**) **2**; (**g**) [*m*-$C_{12}Br_2$]; (**h**) [*m*-$C_{12}(NTf_2)_2$] (exo up).



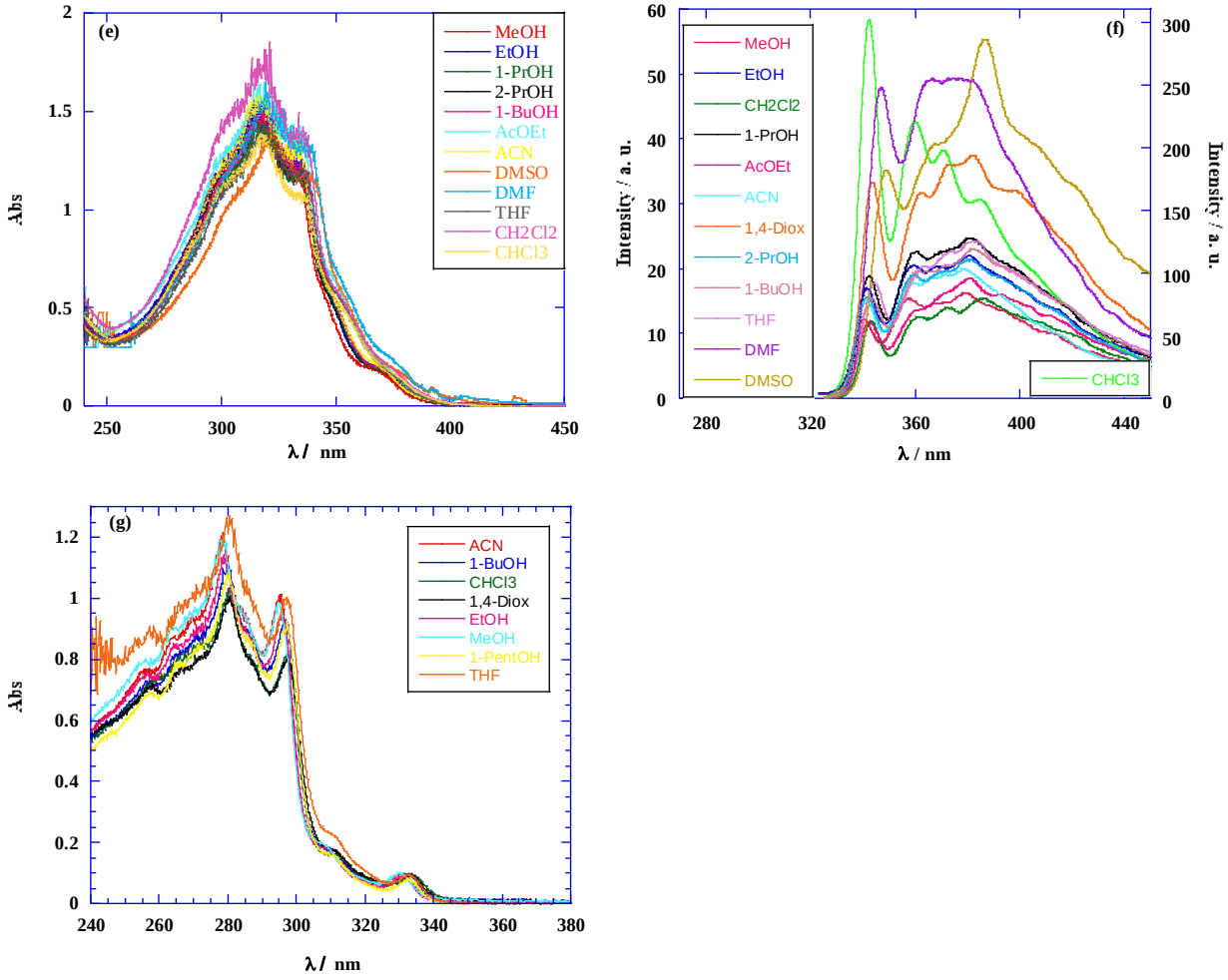
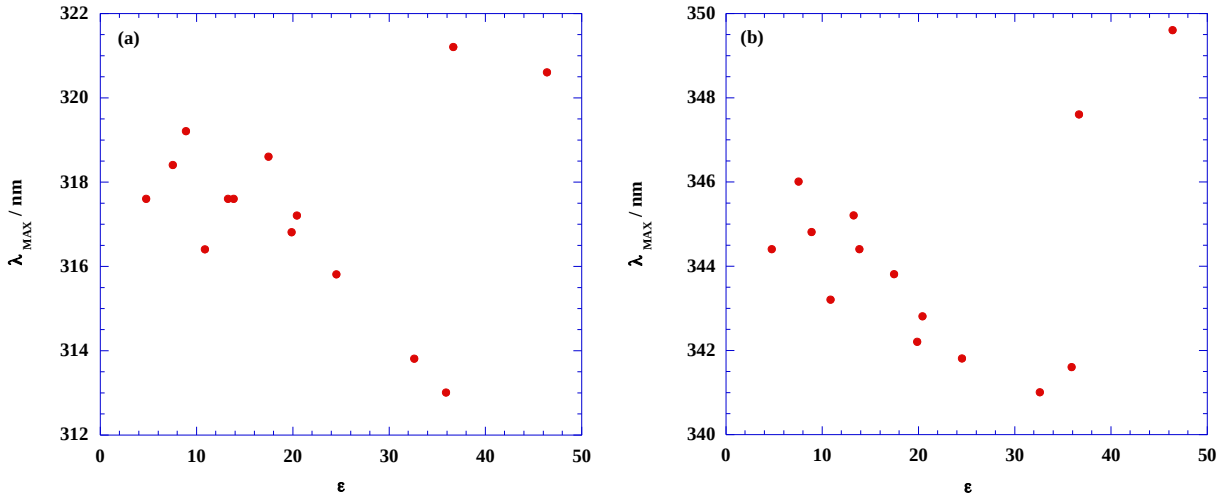
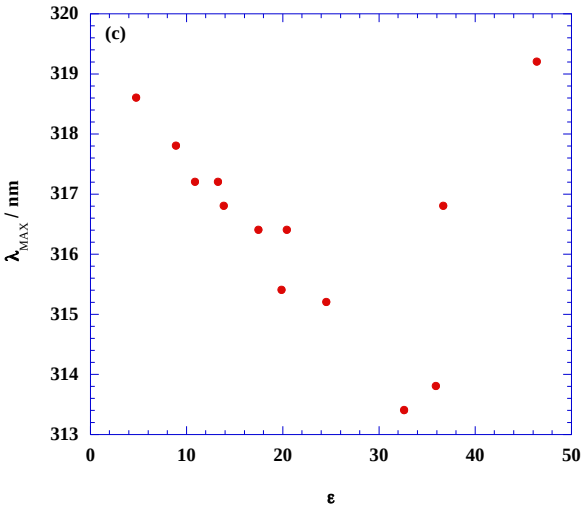
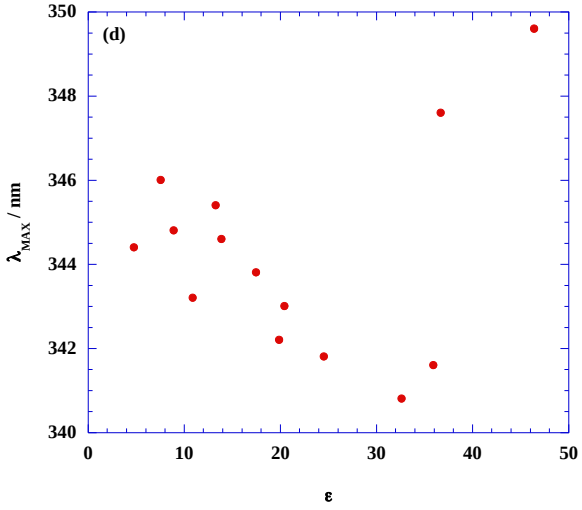


Fig. S3 UV-vis and fluorescence spectra recorded in different solvents at 298 K for: (**a**) and (**b**) [*p*-C_8Br_2]; (**c**) and (**d**) [*p*-$C_{12}Br_2$]; (**e**) and (**f**) [*p*-$C_8(NTf_2)_2$]; (**g**) [*m*-$C_{12}(NTf_2)_2$].




(c)
320
319
318
317
316
315
314
313
0
10
20
30
40
50
ε
λMAX / nm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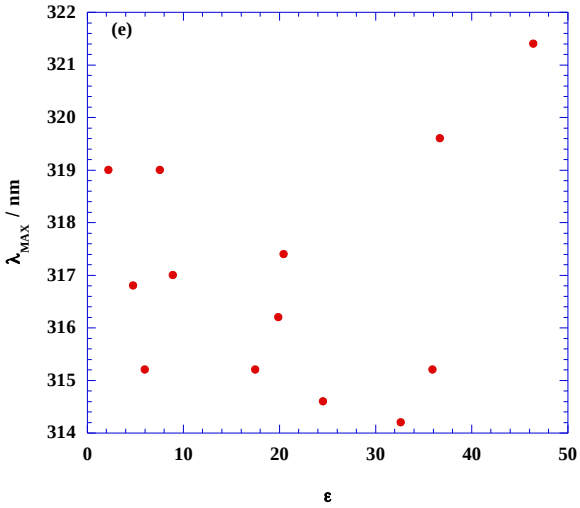
348
346
344
342
340
0
10
20
30
40
50
ε
λMAX / nm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320
319
318
317
316
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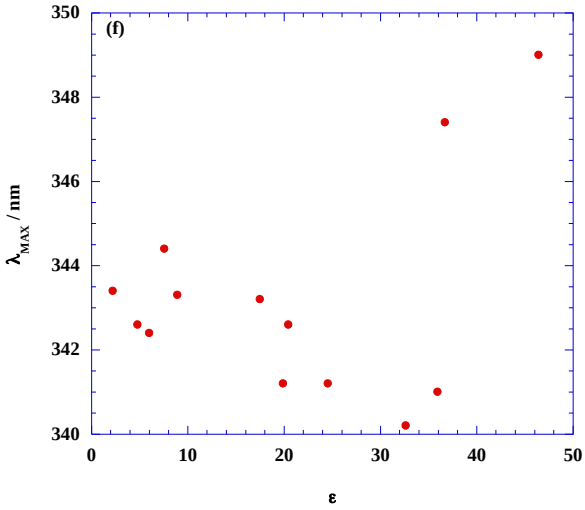
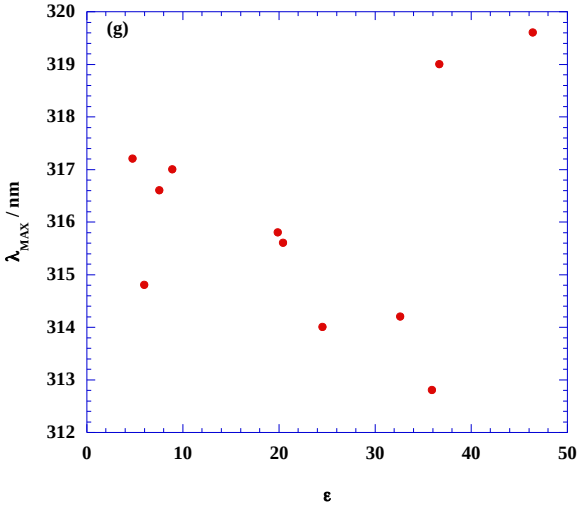
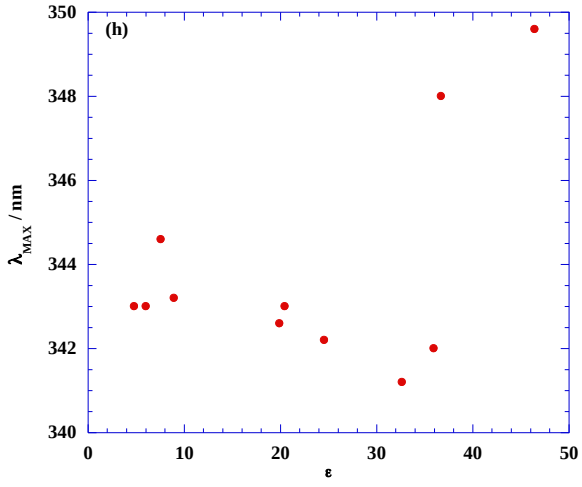
314
0
10
20
30
40
50
ε
λMAX / nm


(f)
350
348
346
344
342
340
0
10
20
30
40
50
ε
λMAX / nm


(g)
320
319
318
317
316
315
314
313
312
0
10
20
30
40
50
ε
λMAX / nm


(h)
350
348
346
344
342
340
0
10
20
30
40
50
ε
λMAX / nm

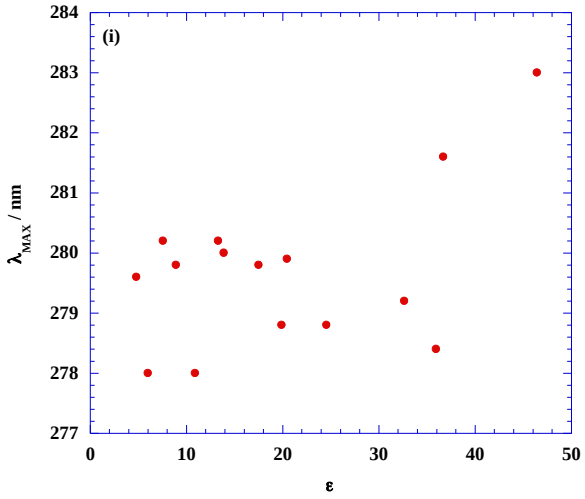
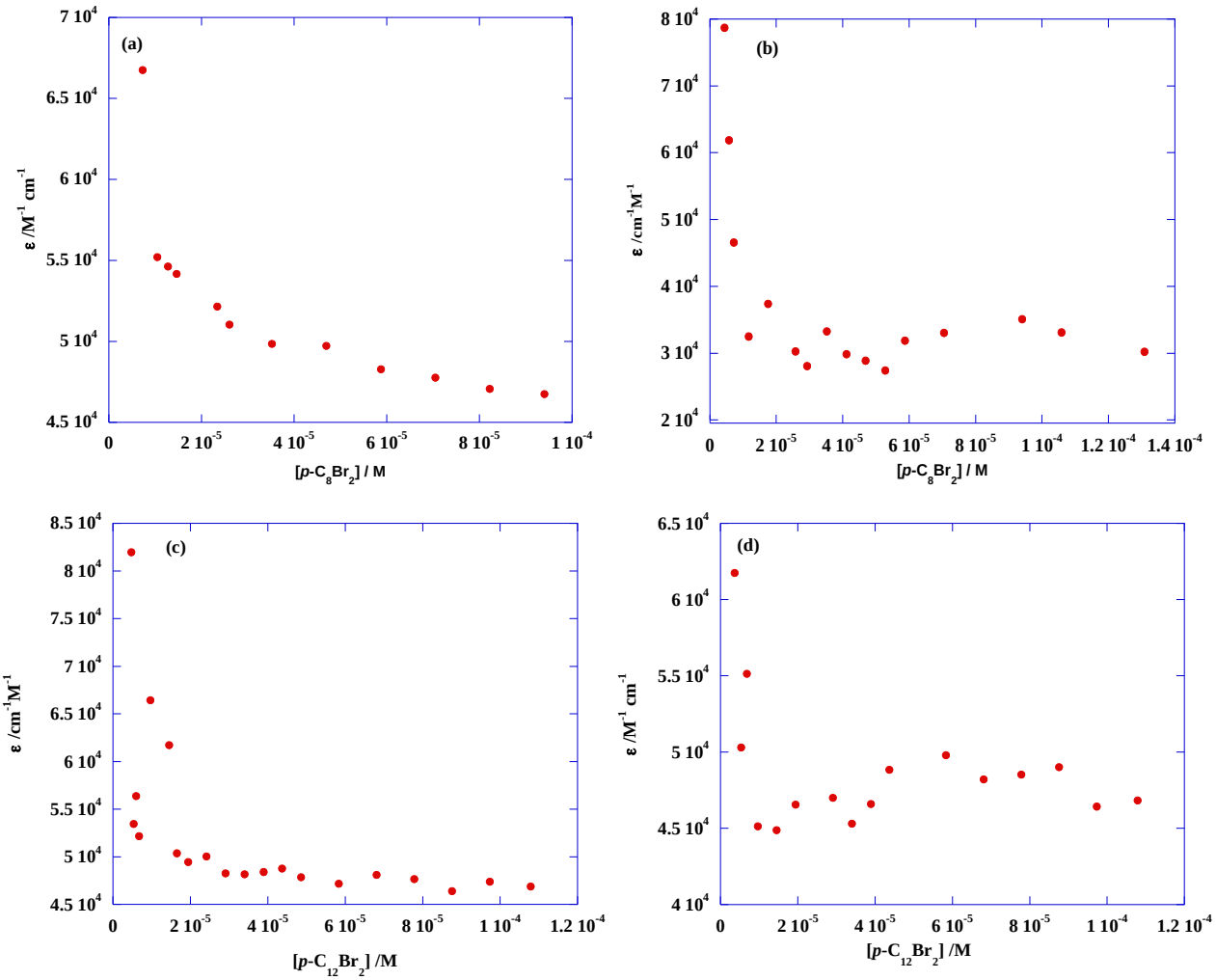
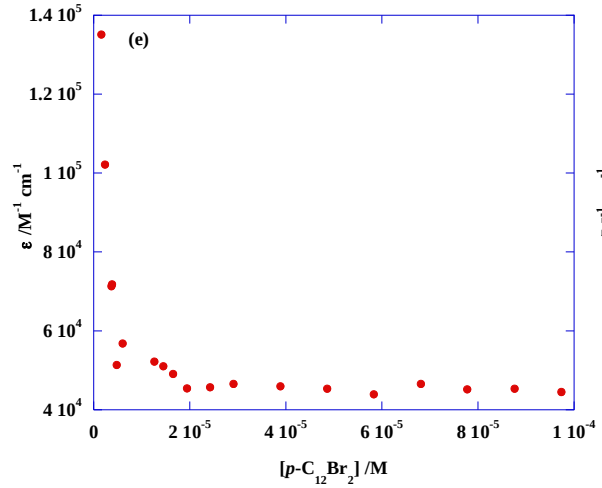
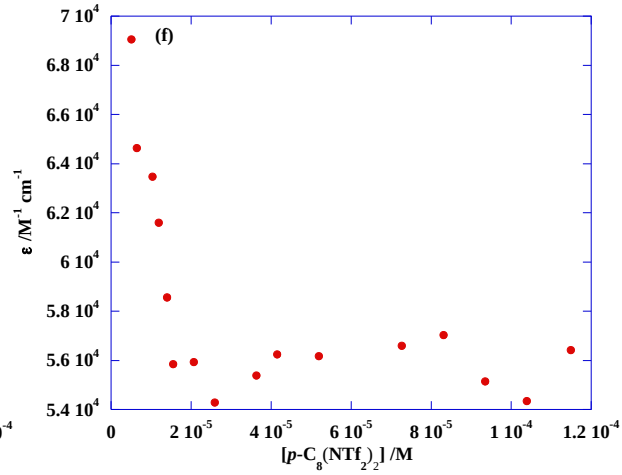
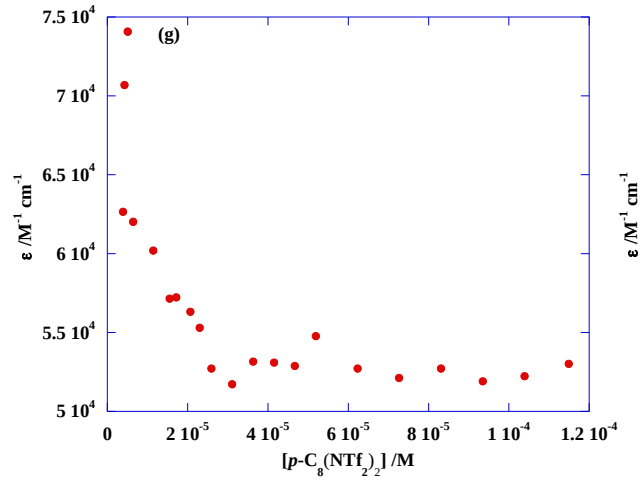


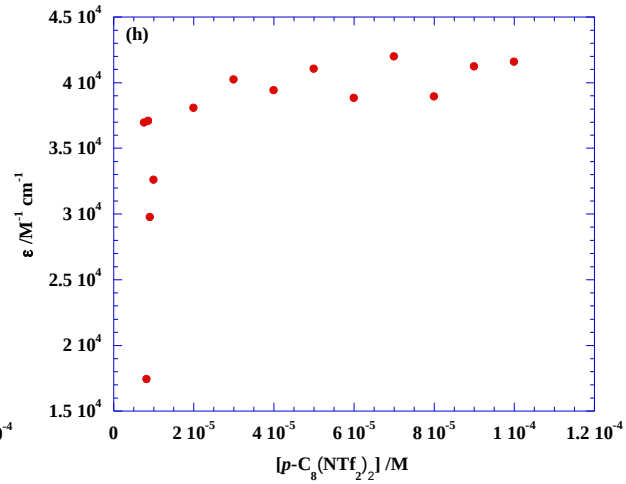
Fig. S4 Plots of UV-vis and fluorescence maxima (λ_{MAX}) recorded in different solvents at 298 K for: (**a**) and (**b**) [*p*-C_8Br_2]; (**c**) and (**d**) [*p*-$C_{12}Br_2$]; (**e**) and (**f**) [*p*-$C_8(NTf_2)_2$]; (**g**) and (**h**) [*p*-$C_{12}(NTf_2)_2$]; (**i**) *m*-$C_{12}(NTf_2)_2$].

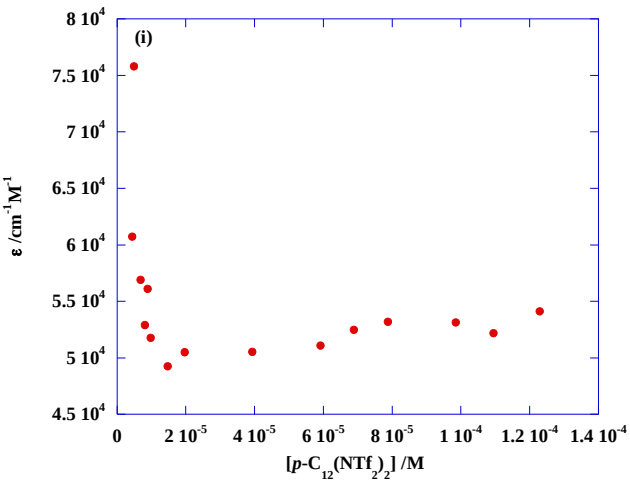


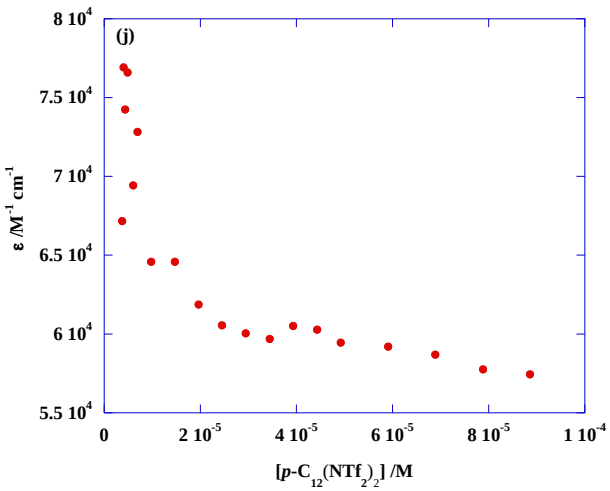

(e)
ε /M-1 cm-1
[p-C12Br2] /M


(f)
ε /M-1 cm-1
[p-C8(NTf2)2] /M


(g)
ε /M-1 cm-1
[p-C8(NTf2)2] /M


(h)
ε /M-1 cm-1
[p-C8(NTf2)2] /M


(i)
ε /cm-1M-1
[p-C12(NTf2)2] /M


(j)
ε /M-1 cm-1
[p-C12(NTf2)2] /M

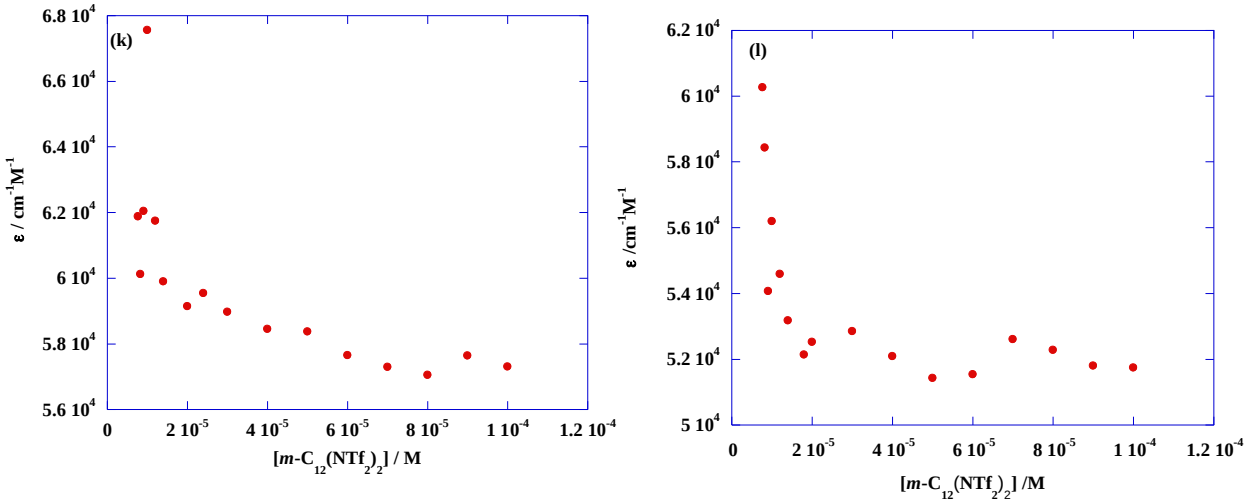
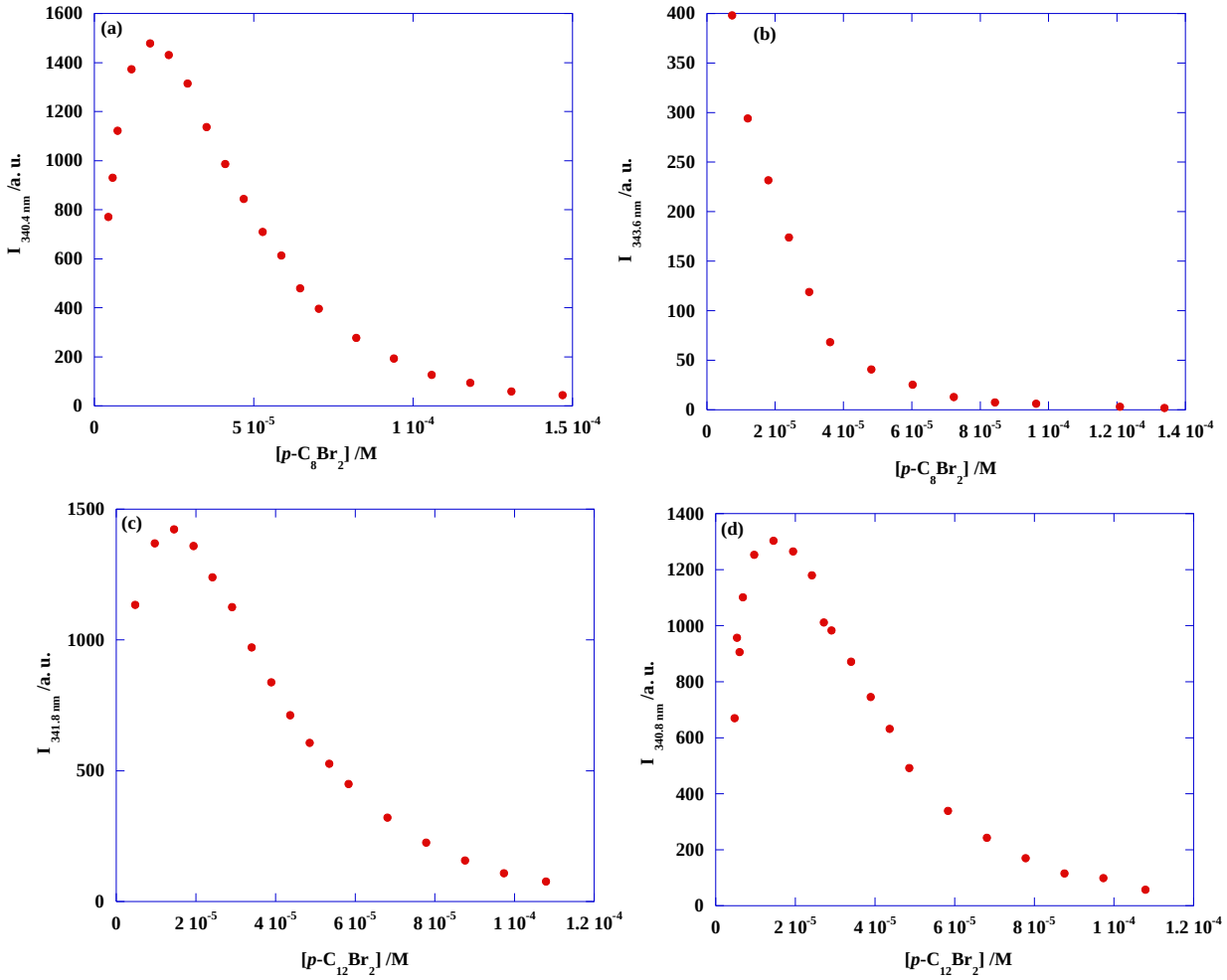


Fig. S5 Plots of apparent absorption coefficient as a function of salt concentration corresponding to: (**a**) [*p*-C_8Br_2] in ACN; (**b**) [*p*-C_8Br_2] in THF; (**c**) [*p*-$C_{12}Br_2$] in 1-PrOH; (**d**) [*p*-$C_{12}Br_2$] in 2-PrOH; (**e**) [*p*-$C_{12}Br_2$] in $CHCl_3$; (**f**) [*p*-$C_8(NTf_2)_2$] in 2-PrOH; (**g**) [*p*-$C_8(NTf_2)_2$] in $CHCl_3$; (**h**) [*p*-$C_8(NTf_2)_2$] in 1,4-Diox; (**i**) [*p*-$C_{12}(NTf_2)_2$] in ACN; (**j**) [*p*-$C_{12}(NTf_2)_2$] in THF; (**k**) [*m*-$C_{12}(NTf_2)_2$] in 1-PrOH; (**l**) [*m*-$C_{12}(NTf_2)_2$] in $CHCl_3$.



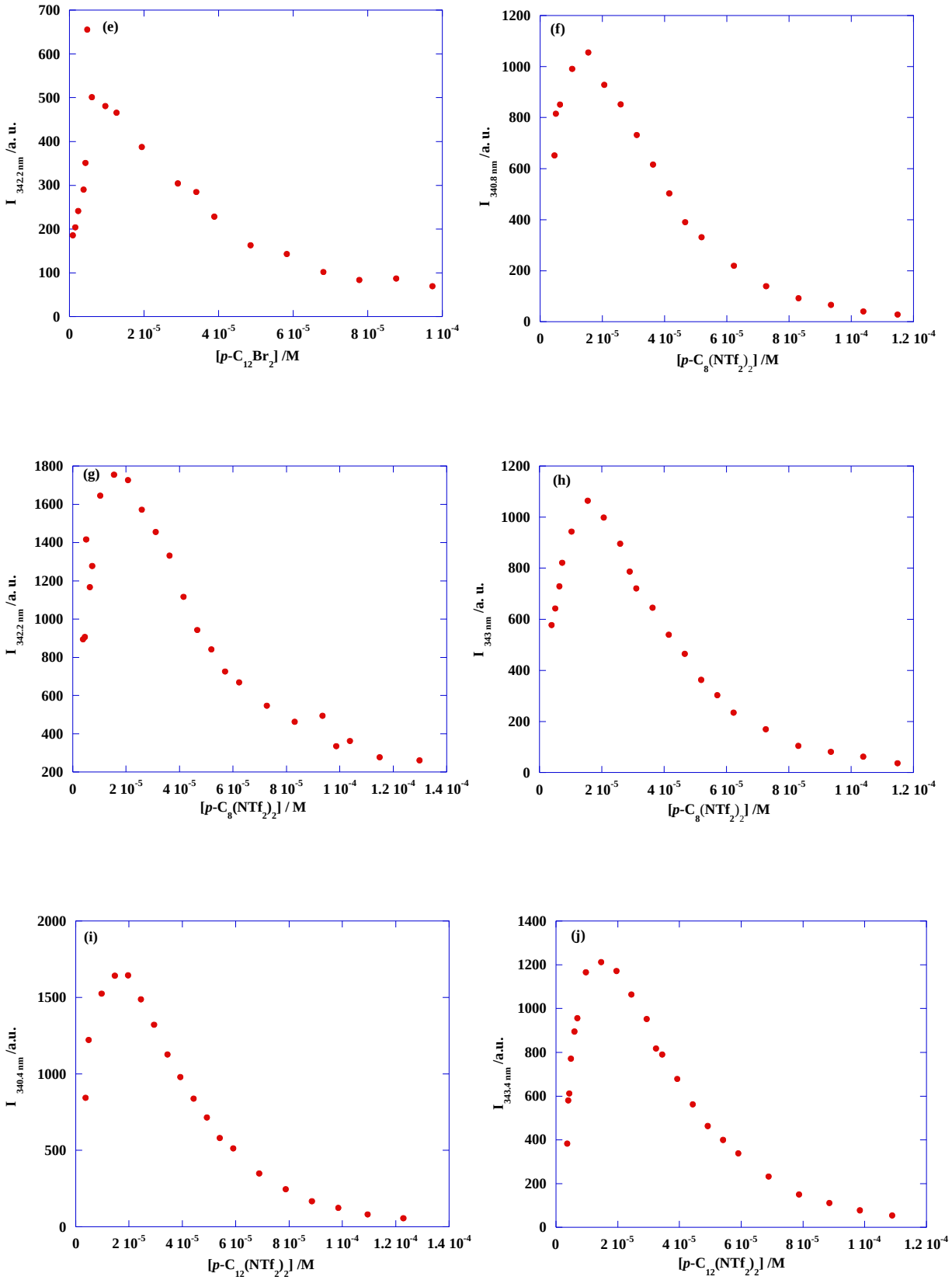
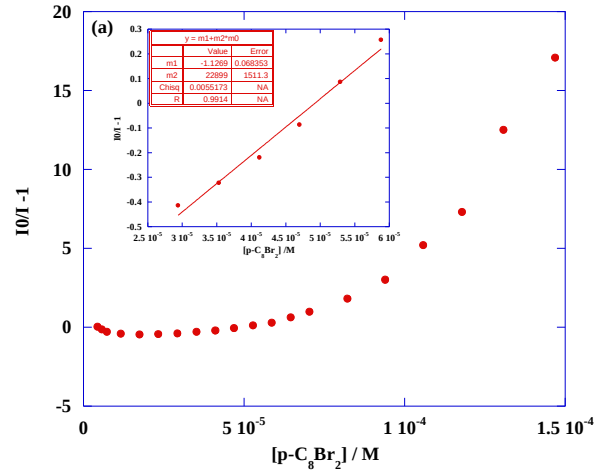
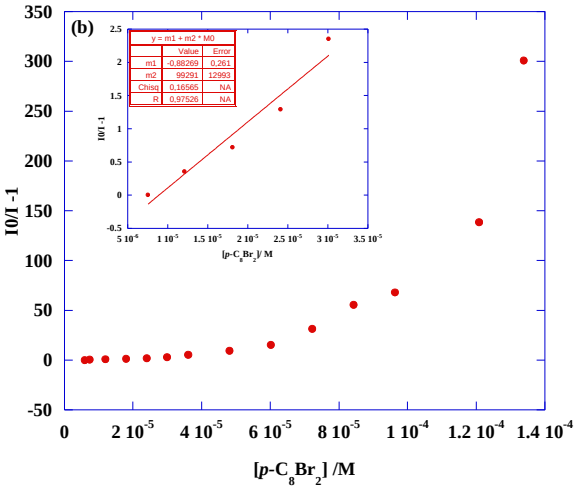
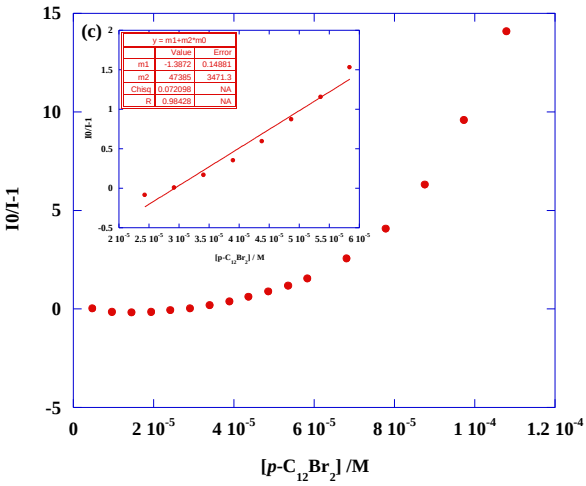
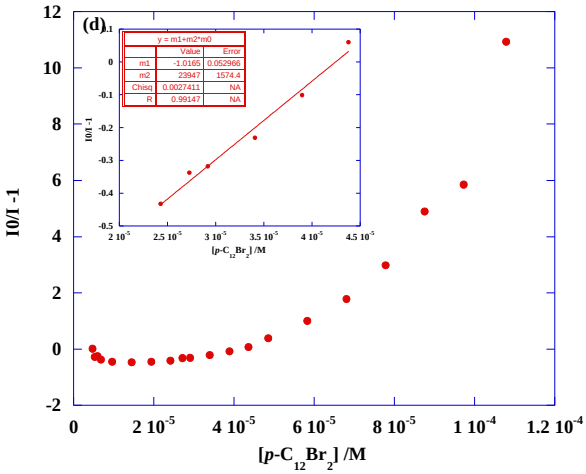


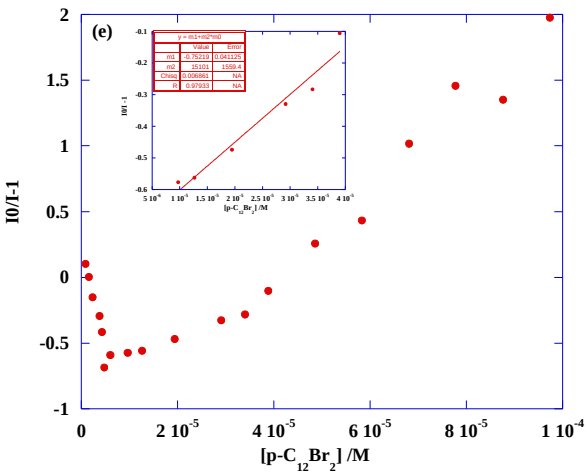
Fig. S6 Plots of fluorescence intensity as a function of salt concentration corresponding to: (**a**) [*p*-C_8Br_2] in ACN; (**b**) [*p*-C_8Br_2] in THF; (**c**) [*p*-$C_{12}Br_2$] in 1-PrOH; (**d**) [*p*-$C_{12}Br_2$] in 2-PrOH; (**e**) [*p*-$C_{12}Br_2$] in $CHCl_3$; (**f**) [*p*-$C_8(NTf_2)_2$] in 2-PrOH; (**g**) [*p*-$C_8(NTf_2)_2$] in $CHCl_3$; (**h**) [*p*-$C_8(NTf_2)_2$] in 1,4-Diox; (**i**) [*p*-$C_{12}(NTf_2)_2$] in ACN; (**j**) [*p*-$C_{12}(NTf_2)_2$] in THF.

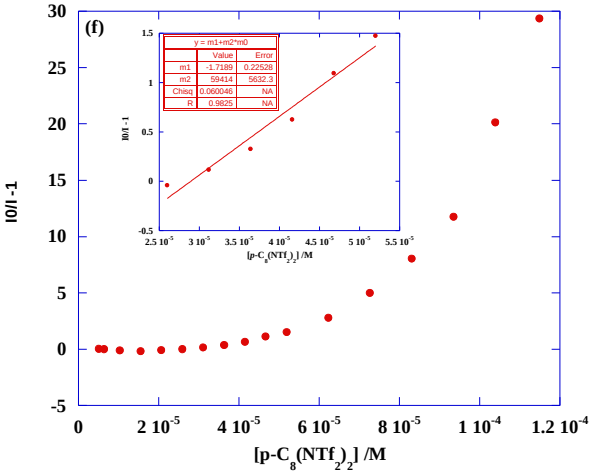

(a)
I0/I -1
[p-C8Br2] / M


(b)
I0/I -1
[p-C8Br2] /M


(c)
I0/I-1
[p-C12Br2] /M


(d)
I0/I -1
[p-C12Br2] /M


(e)
I0/I-1
[p-C12Br2] /M


(f)
I0/I -1
[p-C8(NTf2)2] /M

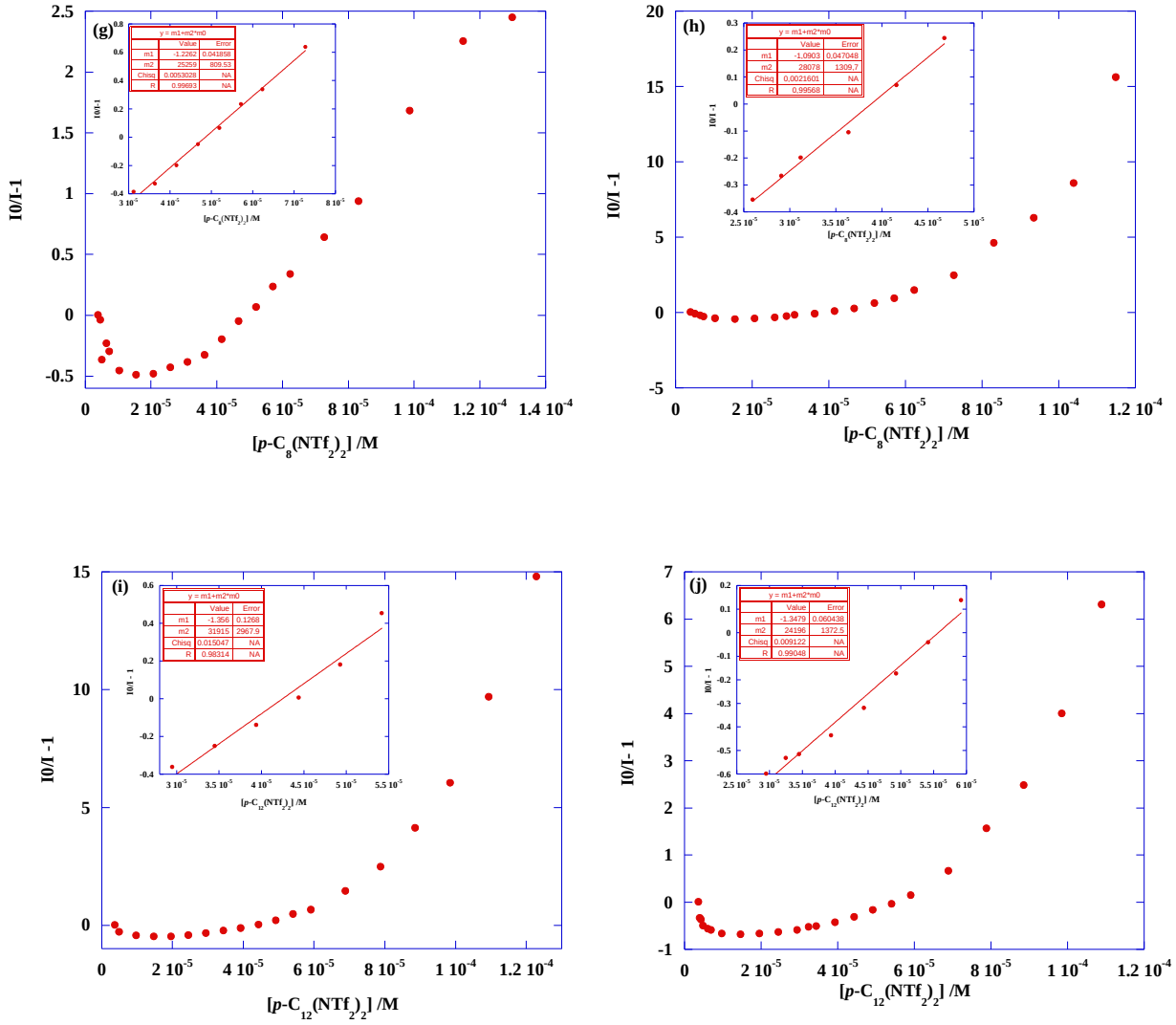
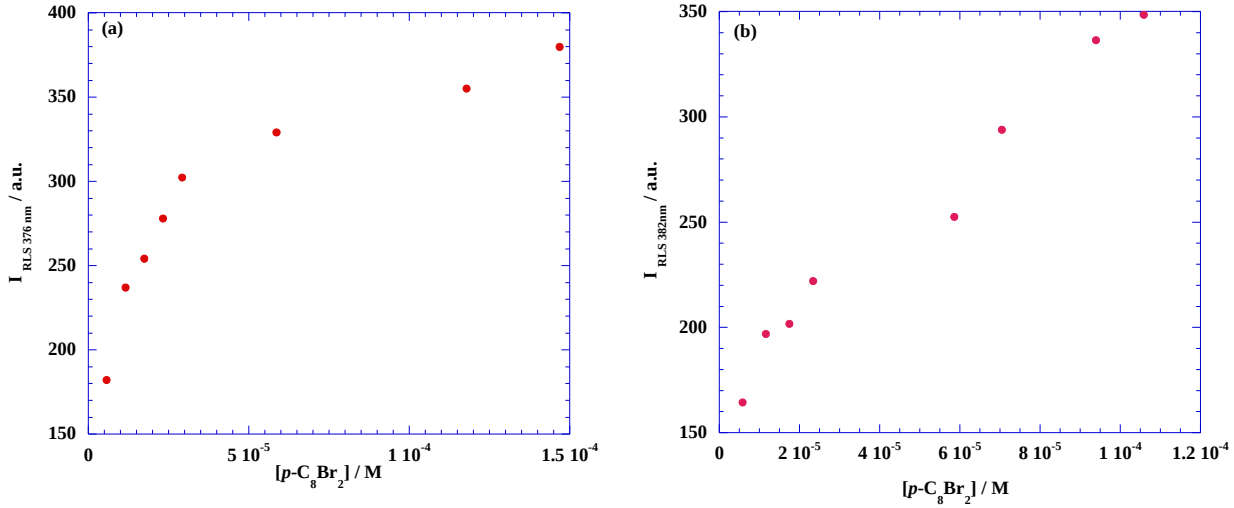
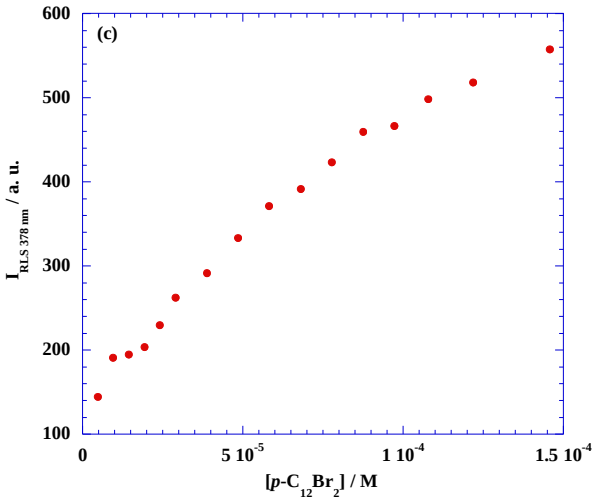
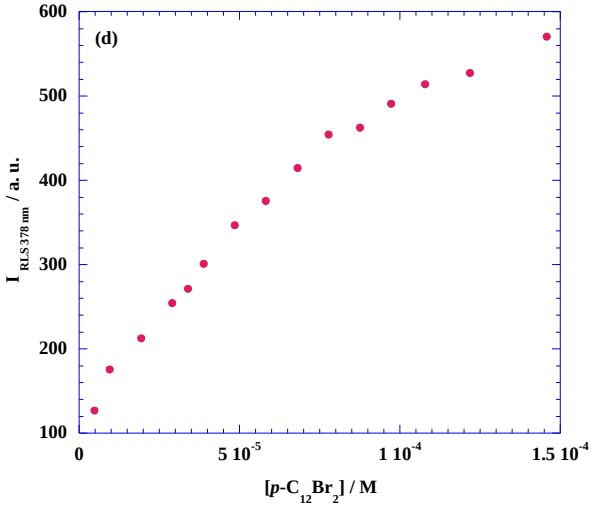
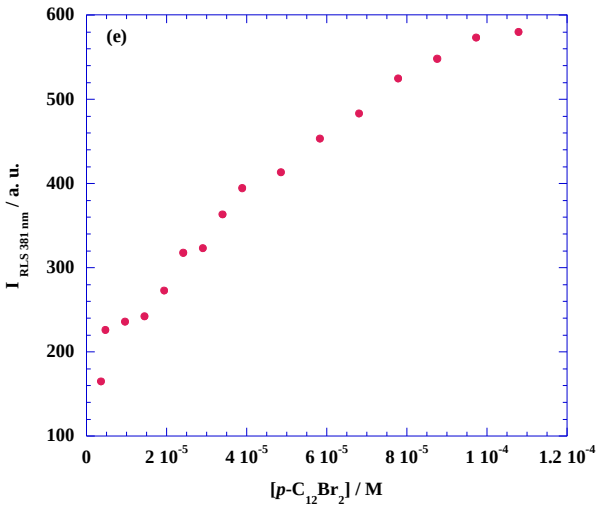


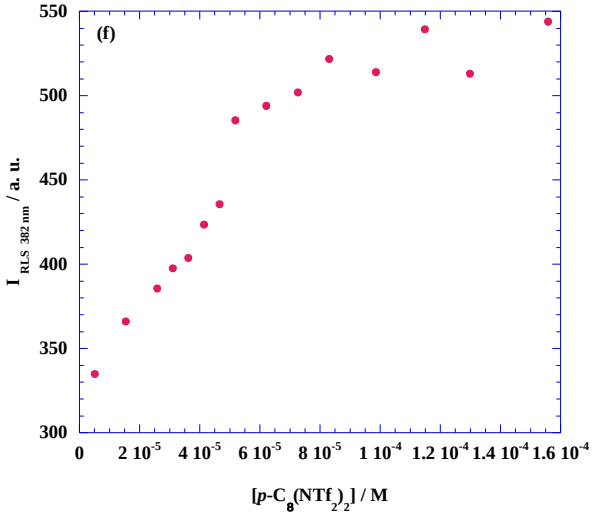
Fig. S7 Stern-Volmer plots corresponding to: (**a**) [*p*-C_8Br_2] in ACN; (**b**) [*p*-C_8Br_2] in THF; (**c**) [*p*-$C_{12}Br_2$] in 1-PrOH; (**d**) [*p*-$C_{12}Br_2$] in 2-PrOH; (**e**) [*p*-$C_{12}Br_2$] in $CHCl_3$; (**f**) [*p*-$C_8(NTf_2)_2$] in 2-PrOH; (**g**) [*p*-$C_8(NTf_2)_2$] in $CHCl_3$; (**h**) [*p*-$C_8(NTf_2)_2$] in 1,4-Diox; (**i**) [*p*-$C_{12}(NTf_2)_2$] in ACN; (**j**) [*p*-$C_{12}(NTf_2)_2$] in THF.

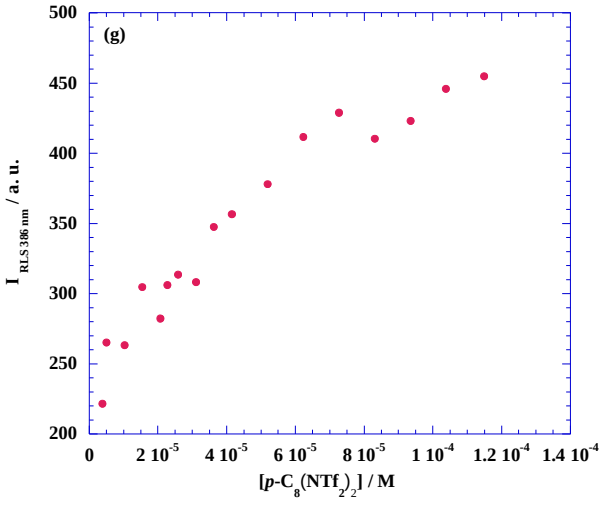


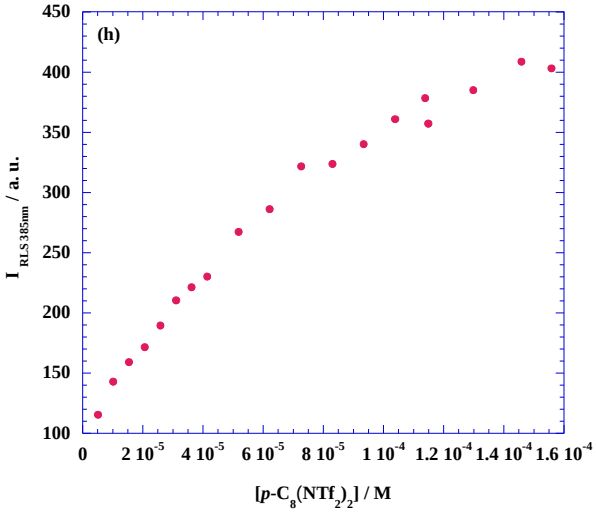

(c)
600
500
400
300
200
100
0
5 10-5
1 10-4
1.5 10-4
I RLS 378 nm / a. u.
[p-C12Br2] / M


(d)
600
500
400
300
200
100
0
5 10-5
1 10-4
1.5 10-4
I RLS 378 nm / a. u.
[p-C12Br2] / M


(e)
600
500
400
300
200
100
0
2 10-5
4 10-5
6 10-5
8 10-5
1 10-4
1.2 10-4
I RLS 381 nm / a. u.
[p-C12Br2] / M


(f)
550
500
450
400
350
300
0
2 10-5
4 10-5
6 10-5
8 10-5
1 10-4
1.2 10-4
1.4 10-4
1.6 10-4
I RLS 382 nm / a. u.
[p-C8(NTf2)2] / M


(g)
500
450
400
350
300
250
200
0
2 10-5
4 10-5
6 10-5
8 10-5
1 10-4
1.2 10-4
1.4 10-4
I RLS 386 nm / a. u.
[p-C8(NTf2)2] / M


(h)
450
400
350
300
250
200
150
100
0
2 10-5
4 10-5
6 10-5
8 10-5
1 10-4
1.2 10-4
1.4 10-4
1.6 10-4
I RLS 385nm / a. u.
[p-C8(NTf2)2] / M

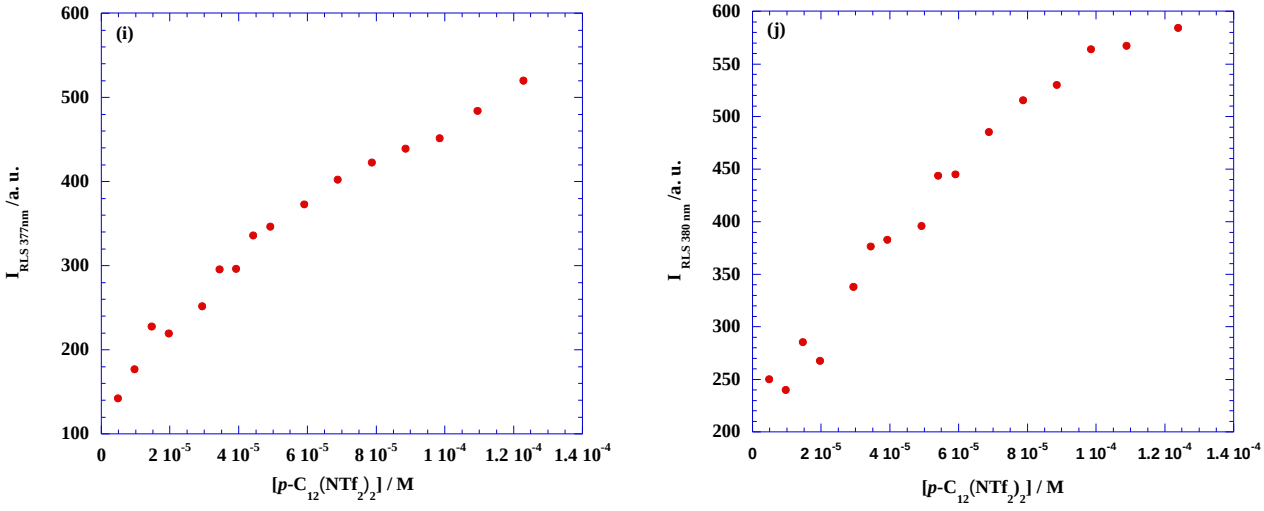
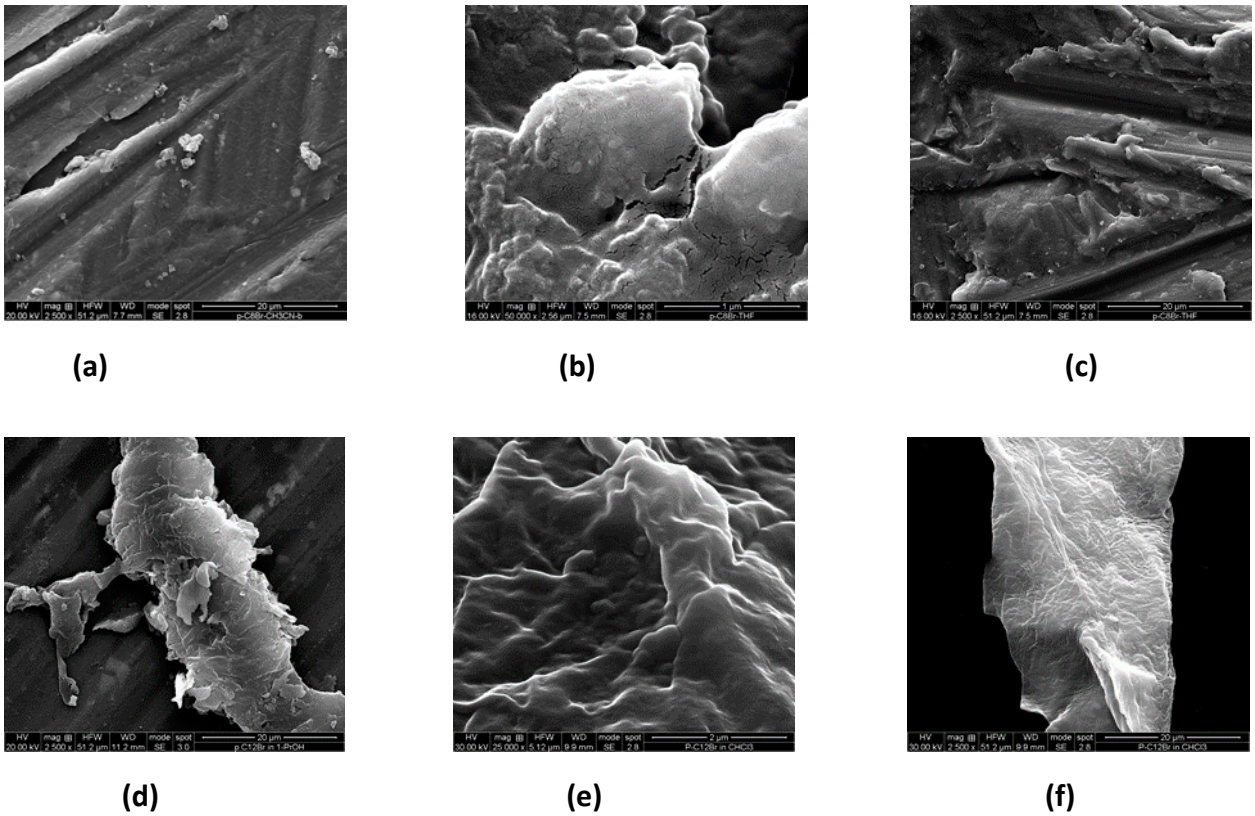


Fig. S8 Plots of RLS intensity as a function of salt concentration corresponding to: (**a**) [*p*-C_8Br_2] in ACN; (**b**) [*p*-C_8Br_2] in THF; (**c**) [*p*-$C_{12}Br_2$] in 1-PrOH; (**d**) [*p*-$C_{12}Br_2$] in 2-PrOH; (**e**) [*p*-$C_{12}Br_2$] in $CHCl_3$; (**f**) [*p*-$C_8(NTf_2)_2$] in 2-PrOH; (**g**) [*p*-$C_8(NTf_2)_2$] in $CHCl_3$; (**h**) [*p*-$C_8(NTf_2)_2$] in 1,4-Diox; (**i**) [*p*-$C_{12}(NTf_2)_2$] in ACN; (**j**) [*p*-$C_{12}(NTf_2)_2$] in THF.



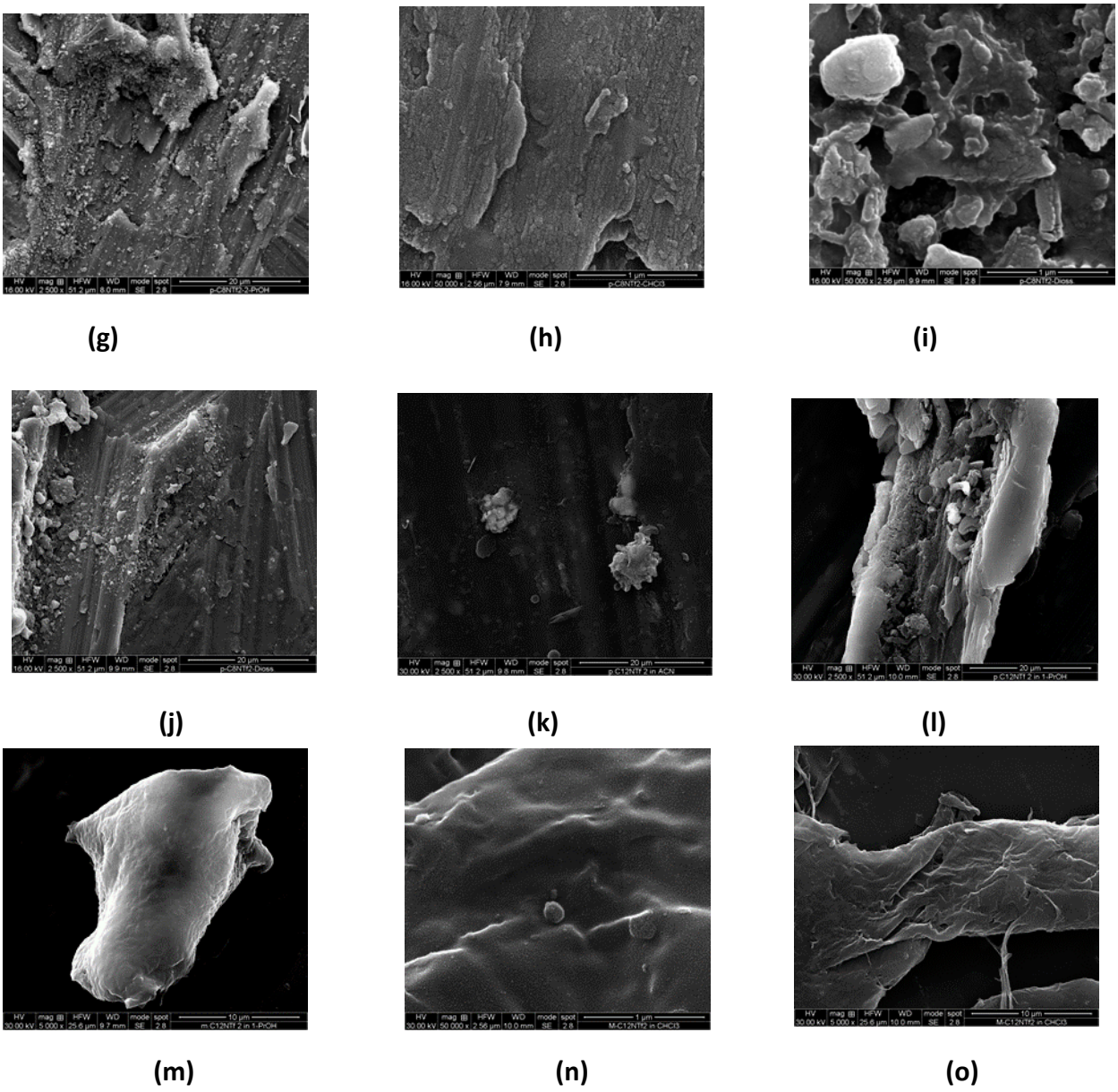
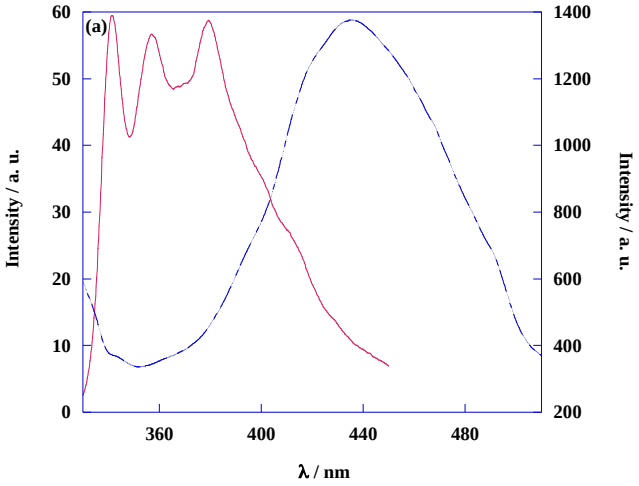
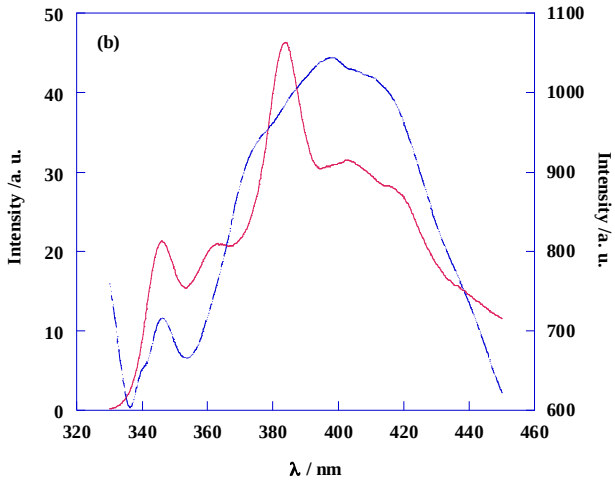
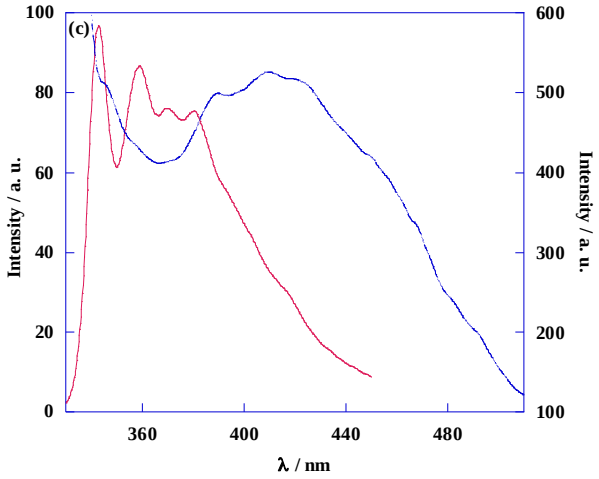
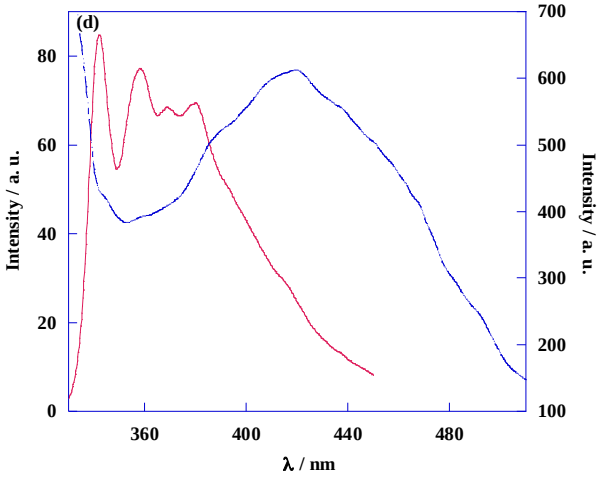


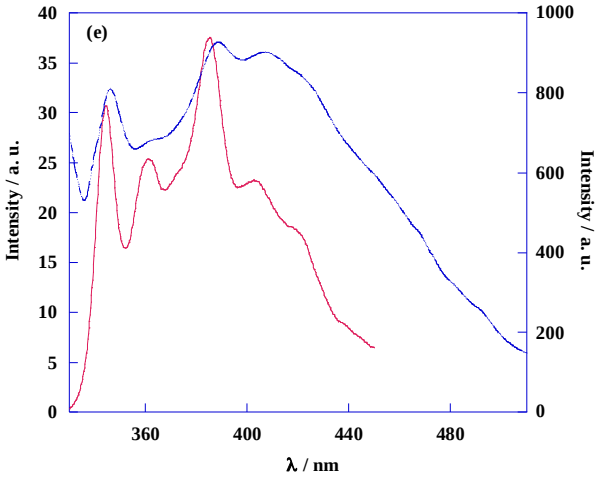
Fig. S9 SEM images collected from casting of 0.0001 M solution. (**a**) [*p*-C_8Br_2]/ACN; (**b**), (**c**) [*p*-C_8Br_2]/THF; (**d**) [*p*-$C_{12}Br_2$]/1-PrOH; (**e**), (**f**) [*p*-$C_{12}Br_2$]/$CHCl_3$; (**g**) [*p*-$C_8(NTf_2)_2$]/2-PrOH; (**h**) [*p*-$C_8(NTf_2)_2$]/$CHCl_3$; (**i**), (**j**) [*p*-$C_8(NTf_2)_2$]/1,4-Diox; (**k**) [*p*-$C_{12}(NTf_2)_2$]/ACN; (**l**) [*p*-$C_{12}(NTf_2)_2$]/1-PrOH; (**m**) [*m*-$C_{12}(NTf_2)_2$]/1-PrOH; (**n**), (**o**) [*m*-$C_{12}(NTf_2)_2$]/$CHCl_3$.

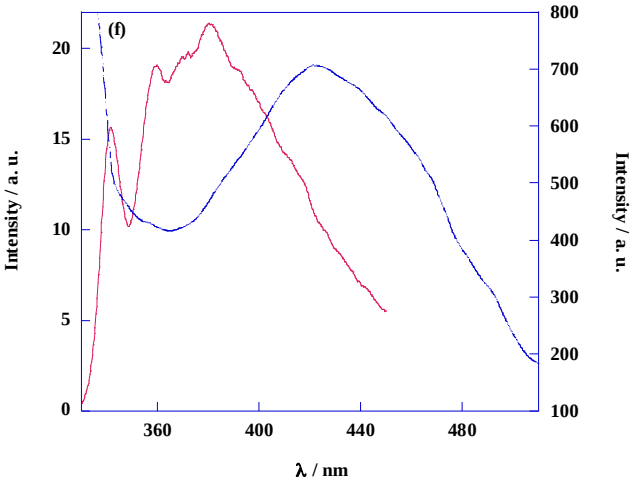

(a)
Intensity / a. u.
Intensity / a. u.
λ / nm


(b)
Intensity /a. u.
Intensity /a. u.
λ / nm


(c)
Intensity / a. u.
Intensity / a. u.
λ / nm


(d)
Intensity / a. u.
Intensity / a. u.
λ / nm


(e)
Intensity / a. u.
Intensity / a. u.
λ / nm


(f)
Intensity / a. u.
Intensity / a. u.
λ / nm

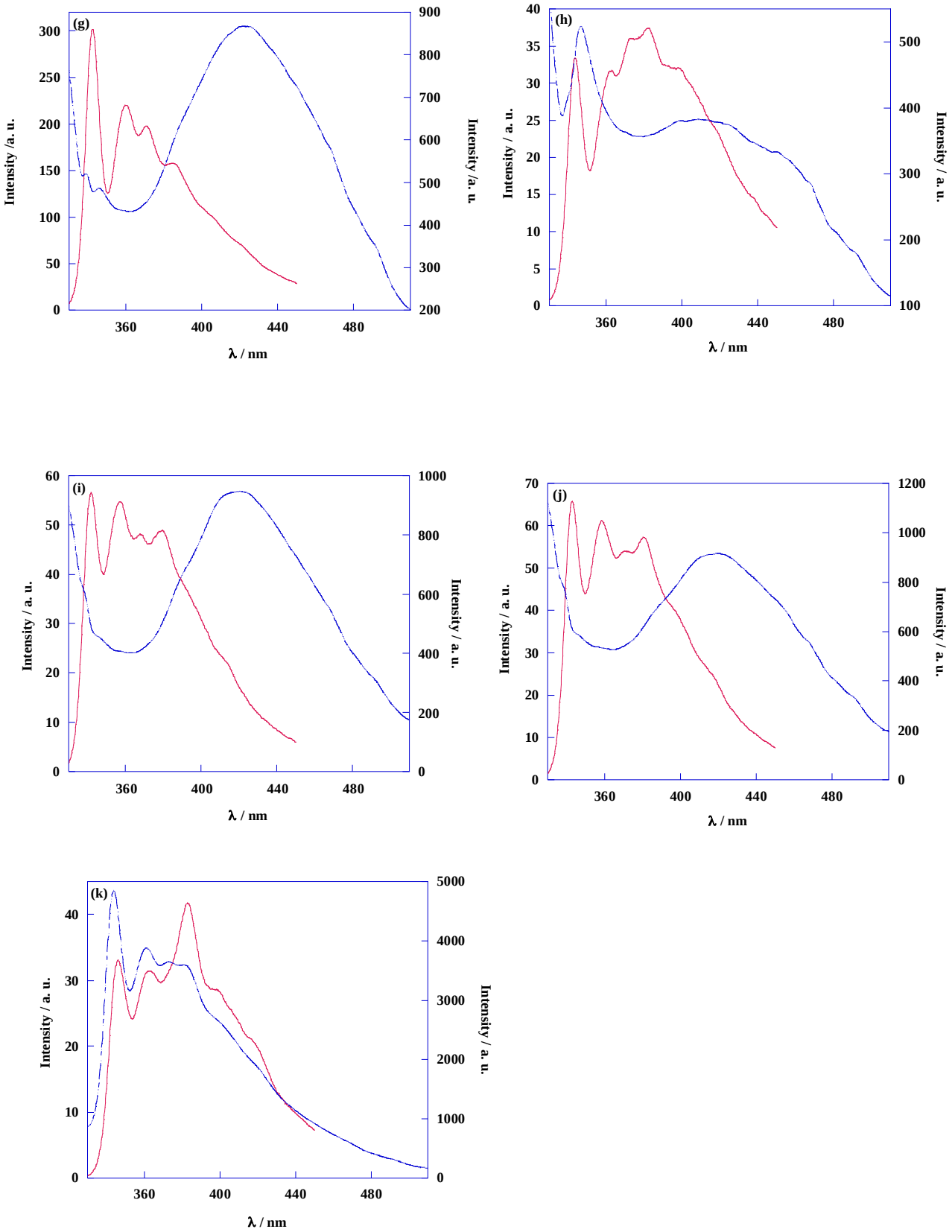


Fig. S10 Fluorescence spectra in solution (red line) and in solid state (blu line) corresponding to: (**a**) [*p*-C_8Br_2] in ACN; (**b**) [*p*-C_8Br_2] in THF; (**c**) [*p*-$C_{12}Br_2$] in 1-PrOH; (**d**) [*p*-$C_{12}Br_2$] in 2-PrOH; (**e**) [*p*-$C_{12}Br_2$] in $CHCl_3$; (**f**) [*p*-$C_8(NTf_2)_2$] in 2-PrOH; (**g**) [*p*-$C_8(NTf_2)_2$] in $CHCl_3$; (**h**) [*p*-$C_8(NTf_2)_2$] in 1,4-Diox; (**i**) [*p*-$C_{12}(NTf_2)_2$] in ACN; (**j**) [*p*-$C_{12}(NTf_2)_2$] in 1-PrOH; (**k**) [*p*-$C_{12}(NTf_2)_2$] in THF.

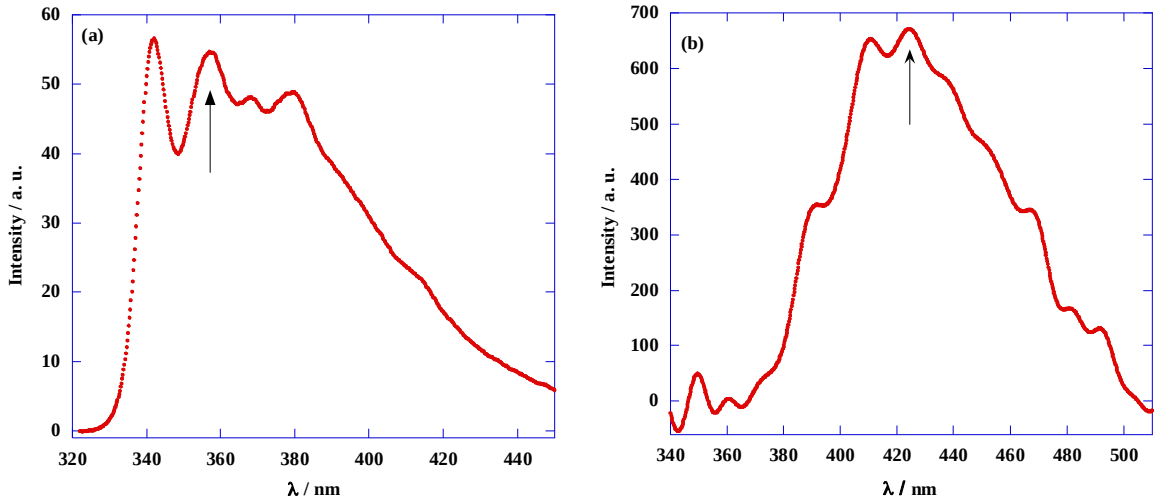


Fig. S11 (a) Solution and **(b)** deconvoluted solid state spectra for [*p*-$C_{12}(NTf_2)_2$].

Table S1 RLS Intensity at 378 nm as function of salt and solvent nature ([salt] = $1 \cdot 10^{-4}$ M).

Salt	Solvent	$I_{RLS\ 378\ nm}$
[*p*-C_8Br_2]	ACN	355
	THF	348
[*p*-$C_{12}Br_2$]	1-PrOH	500
	2-PrOH	514
	$CHCl_3$	576
[*p*-$C_8(NTf_2)_2$]	2-PrOH	540
	$CHCl_3$	440
	1,4-Diox	380
[*p*-$C_{12}(NTf_2)_2$]	ACN	480
	1-PrOH	504
	THF	565

Table S2 Estimated size of solvent molecules on the base of DFT geometries and AMBER atomic radii

Solvent	CAC	a	b	c	m/M
$CHCl_3$	0.82	10.0	10.0	4.8	0.48
2-PrOH	1.14	5.8	5.8	3.1	0.53
1,4-Diox	1.33	6.8	6.8	4.0	0.59
THF	1.44	6.0	6.0	4.0	0.67
1-PrOH	1.54	7.5	4.0	4.0	0.53
ACN	2.00	5.8	2.1	2.1	0.36

a,b and c are dimensions defining ellipsoid shape: a=b>c for a oblate ellipsoid, a>b=c for a prolate ellipsoid; m/M is the ratio between the minor and the major axis.

Table S3 λ_{MAX} and $\Delta\lambda$ values detected for fluorescence spectra recorded in solution and solid state at $1 \cdot 10^{-4}$ M.

Salt	Solvent	$\lambda_{Solution}$/nm	$\lambda_{Solid\ State}$/nm	$\Delta\lambda$/nm
[*p*-C_8Br_2]	ACN	358	434	76
	THF	362	395	33
[*p*-$C_{12}Br_2$]	1-PrOH	358	424	66
	2-PrOH	358	421	63
	$CHCl_3$	360	406	46
[*p*-$C_8(NTf_2)_2$]	2-PrOH	359	422	63
	$CHCl_3$	360	425	65
	1,4-Diox	362	413	51
[*p*-$C_{12}(NTf_2)_2$]	ACN	358	418	60
	1-PrOH	357	419	62
	THF	362	374	12