Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Cation–anion interaction directed dual-mode switchable mechanochromic luminescence

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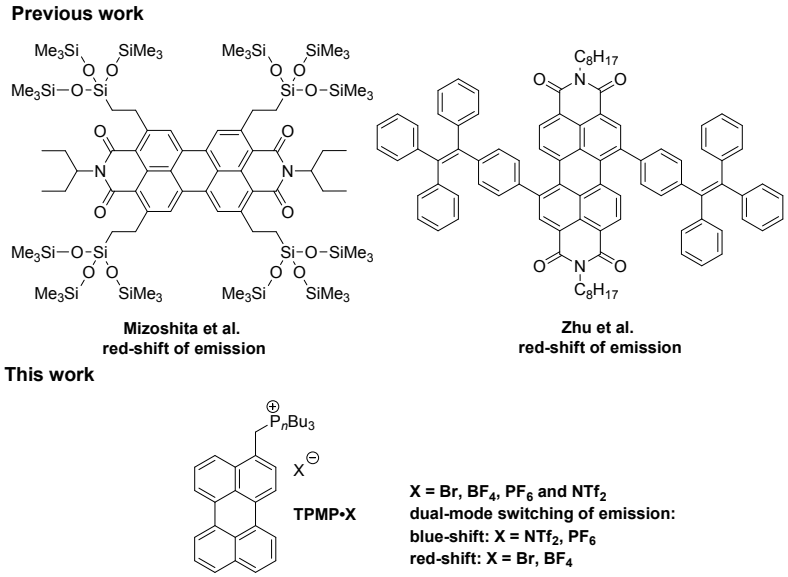
I. Organic mechanochromic luminescent materials based on perylene skeleton



Scheme S1 Organic mechanochromic luminescent materials based on perylene skeleton.

II. X-Ray structure determination

Block crystals of tributyl(perylen-3-ylmethyl)phosphonium bromide (**TPMP·Br**), and tributyl(perylen-3-ylmethyl)phosphonium bis((trifluoromethyl)sulfonyl)amide (**TPMP·NTf$_2$**) were obtained from MeOH/Et$_2$O solutions in refrigerator, respectively. X-Ray single-crystal diffraction data were collected on a Oxford Xcalibur E CCD area-detector diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) with ω scan mode. The crystal parameters, data collection and refinement results for the compound are summarized in Table S1.

Table S1. Crystallographic Data for TPMP·X.

TPMP·X	**TPMP·Br**	**TPMP·PF$_6$**	**TPMP·NTf$_2$**
empirical formula	$C_{33}H_{40}BrP$	$C_{33}H_{40}F_6P_2$	$C_{35}H_{39}F_6NO_4PS_2$
formula weight (M)	547.52	612.59	746.76
temperature (K)	293(2)	133.84(10)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	monoclinic
space group	*P*-1	*P*-2n	*P*-1
a (Å)	18.0756(10)	19.3848(5)	9.7167(3)
b (Å)	9.2768(5)	18.6400(5)	17.3160(6)
c (Å)	19.0097(10)	16.7392(4)	21.7331(7)
α (deg)	90	90	90
β (deg)	95.079(5)	90	102.549(3)
γ (deg)	90	90	90

V (Å^3)	3175.1(3)	6048.4(3)	3569.3(2)
Z	4	8	4
D_{calc} (g cm^{-3})	1.145	1.345	1.390
μ (mm^{-1})	1.362	1.817	0.264
F(000)	1152.0	2576.0	1556.0
crystal size (mm)	0.40×0.35×0.30	0.70×0.40×0.30	0.40×0.20×0.20
reflns collected	14212	18498	18580
unique reflns	6471	5901	7283
R_{int}	0.0232	0.0278	0.0205
R_1, wR_2 (all data)	0.0705, 0.2291	0.1403, 0.4326	0.0939, 0.2986

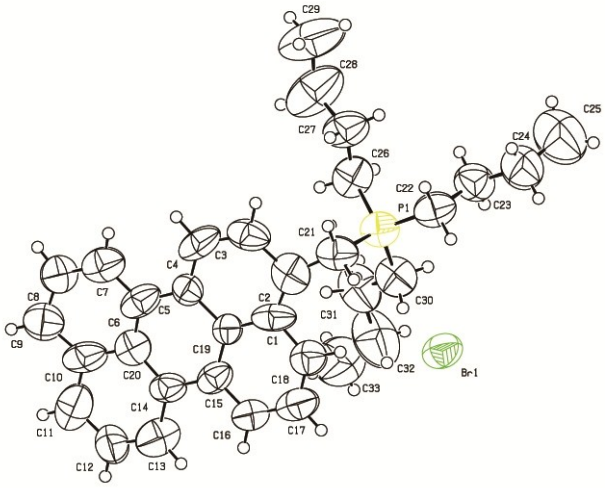


Figure S1. ORTEP drawing of the single crystal of **TPMP·Br** with 50% probability thermal ellipsoids.

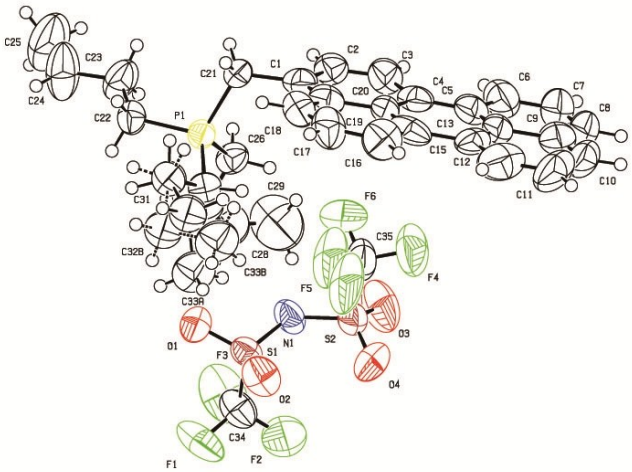


Figure S2. ORTEP drawing of the single crystal of **TPMP·NTf$_2$** with 50% probability thermal ellipsoids.

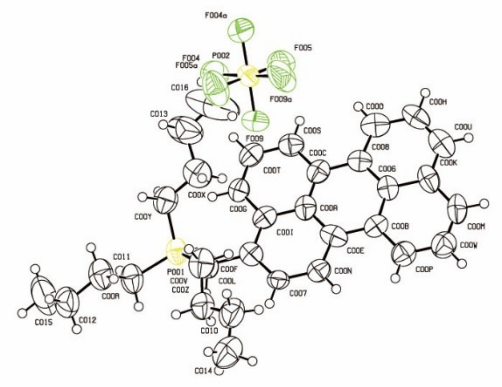


Figure S3. ORTEP drawing of the single crystal of **TPMP·PF_6** with 50% probability thermal ellipsoids.

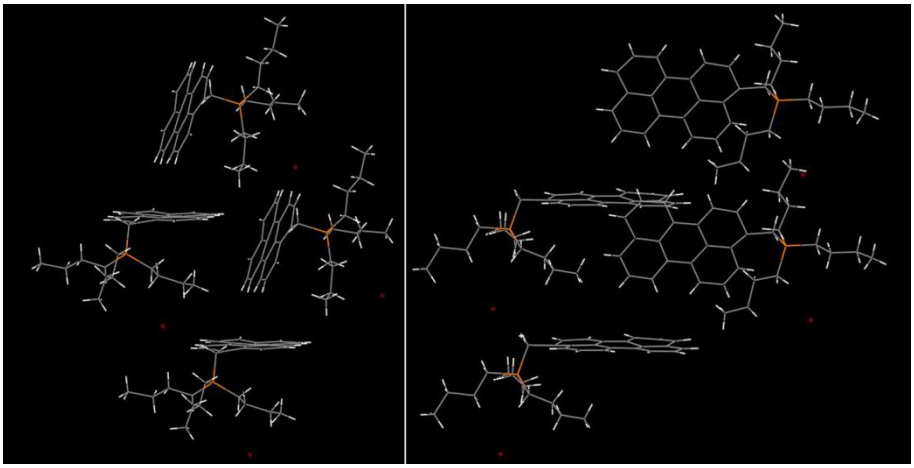


Figure S4. Molecular stacking of the single crystals of **TPMP·Br**: side view (left) and front view (right).

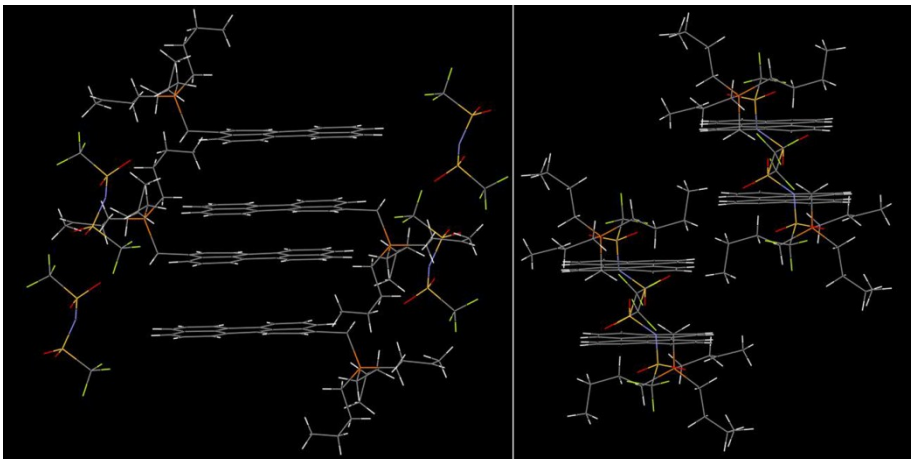


Figure S5. Molecular stacking of the single crystals of **TPMP·NTf_2**: side view (left) and front view (right).

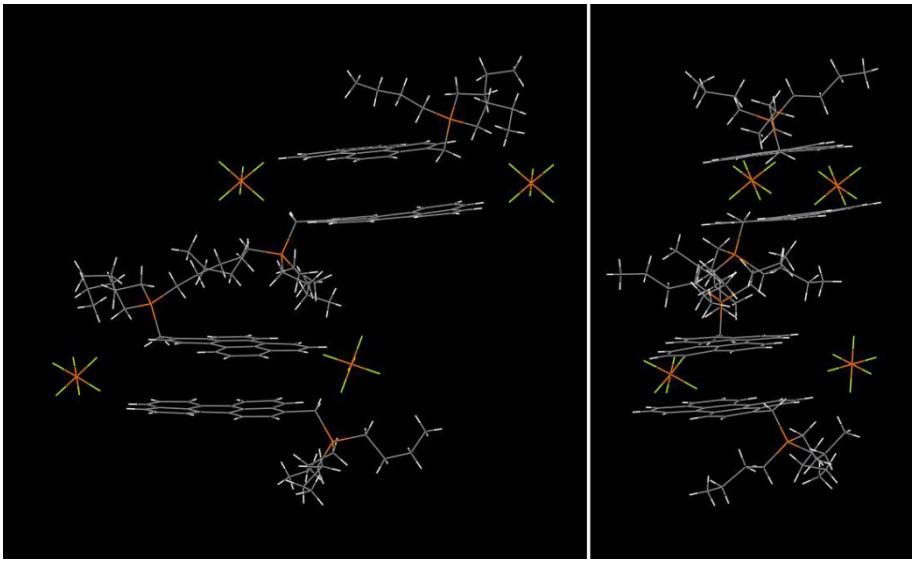


Figure S6. Molecular stacking of the single crystals of **TPMP·PF$_6$**: side view (left) and front view (right).

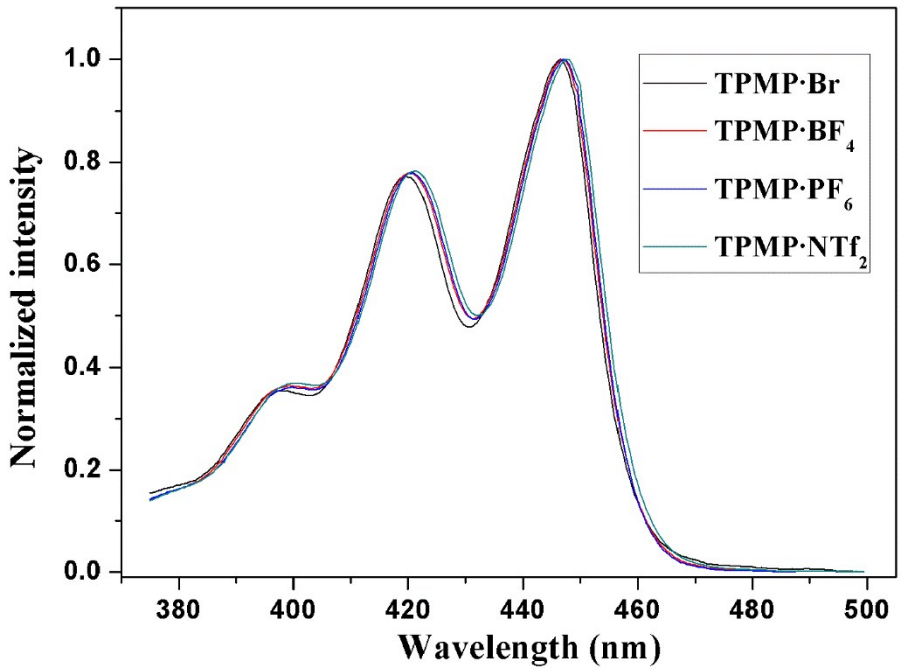


Figure S7. Normalized absorption spectra of phosphonium salts **TPMP·X** (CH_2Cl_2 solution, 5.0 μM).

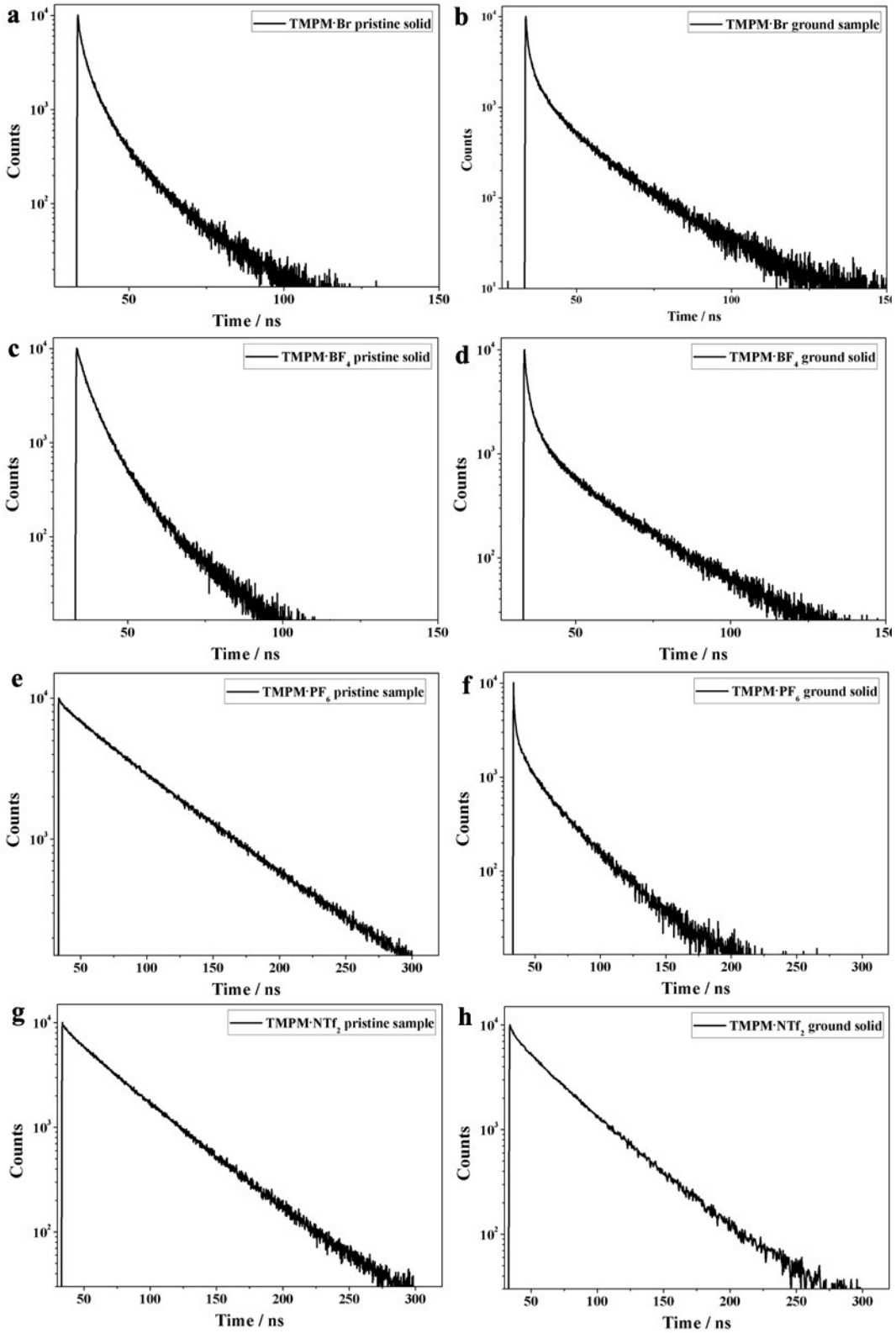
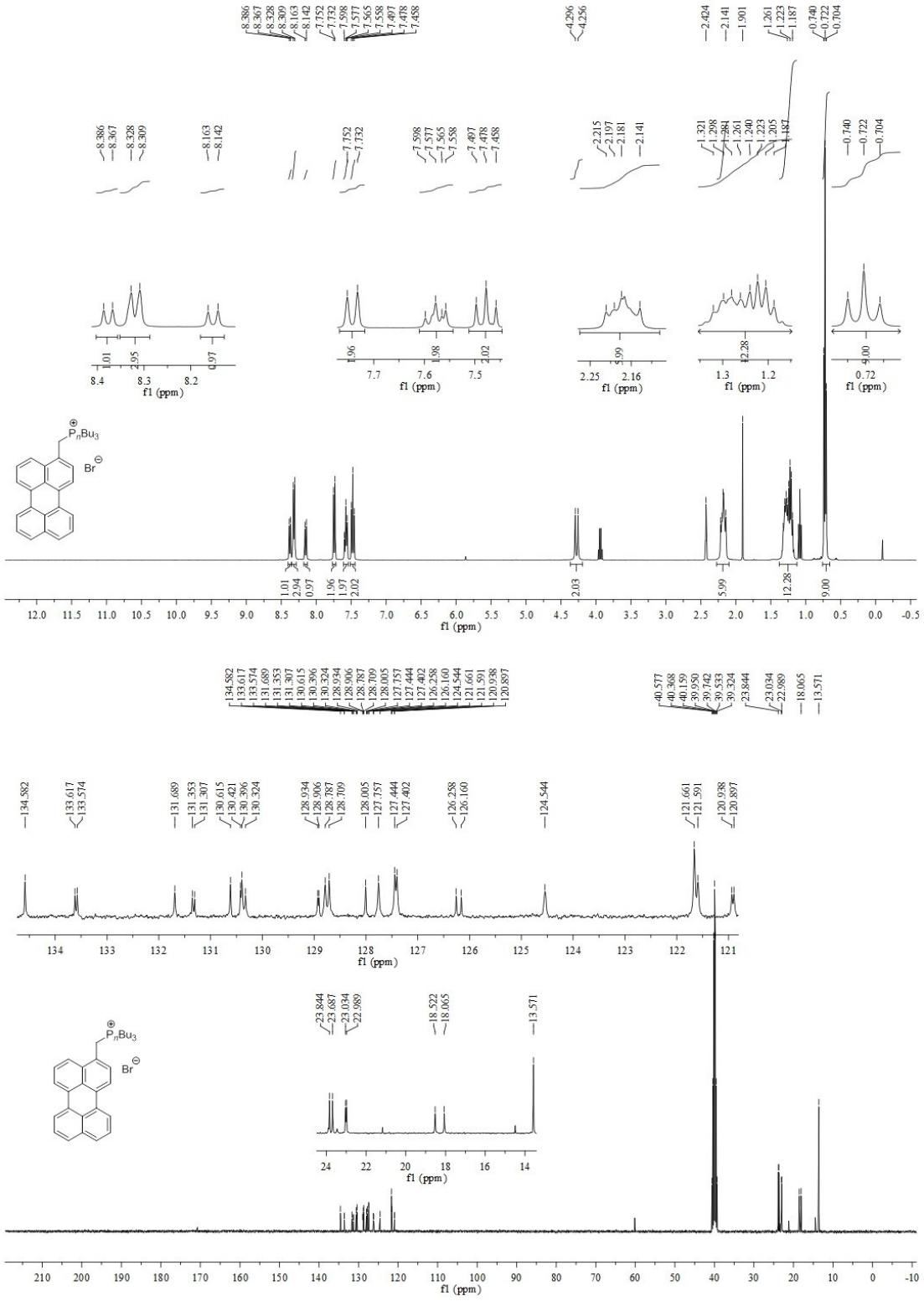
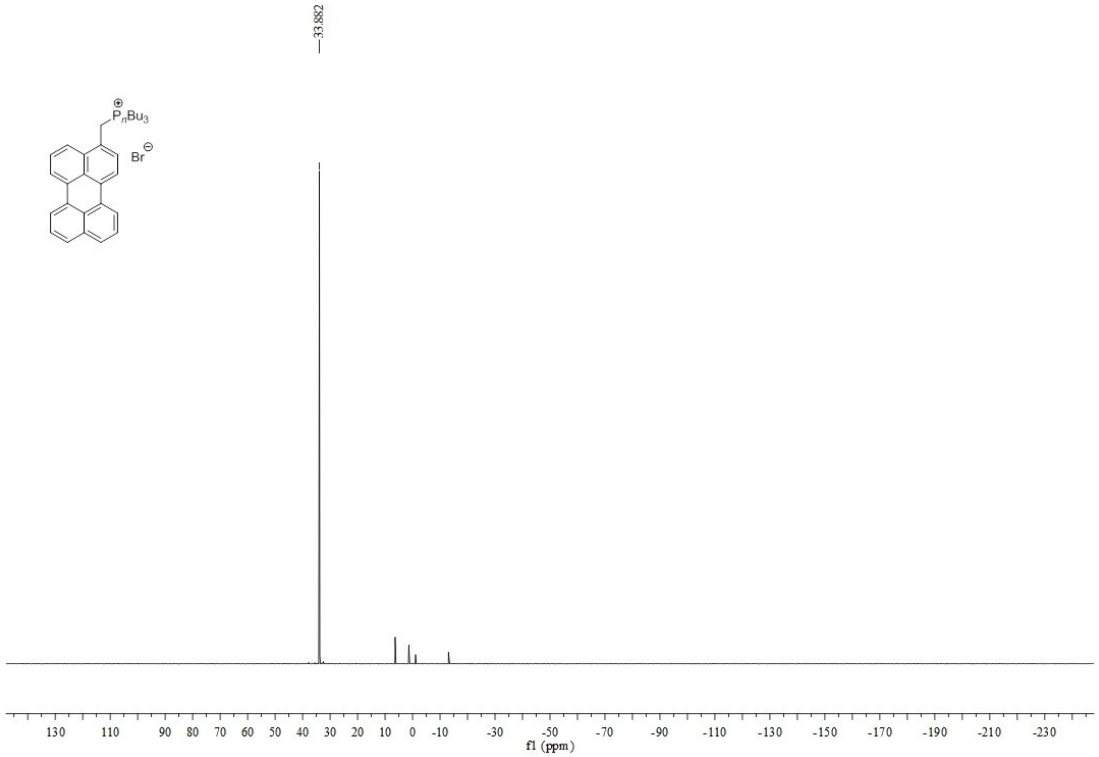
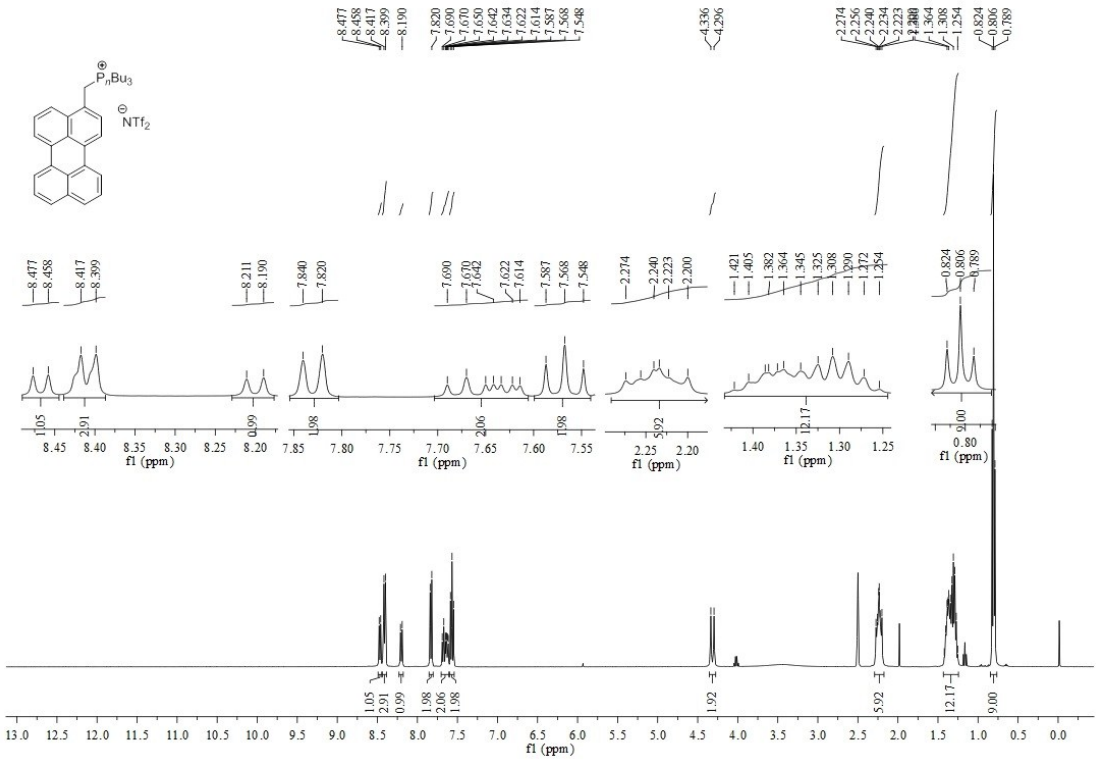


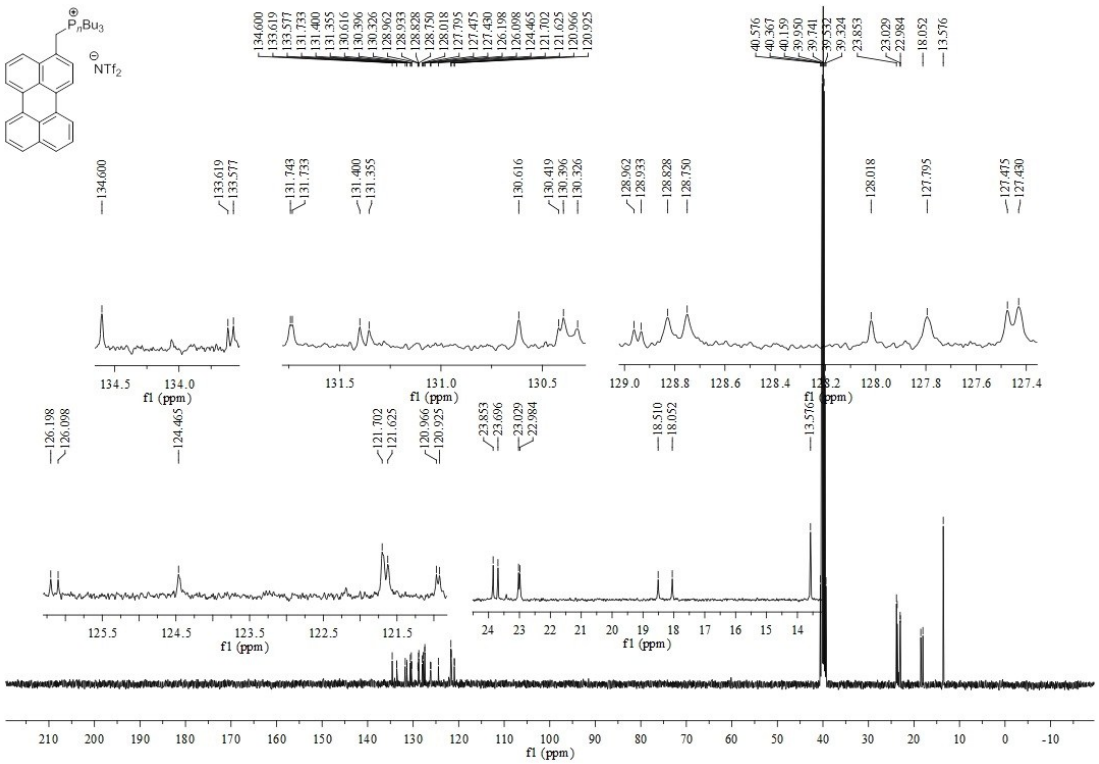
Figure S8. Luminescence decay profiles of **TPMP·X** in different states.

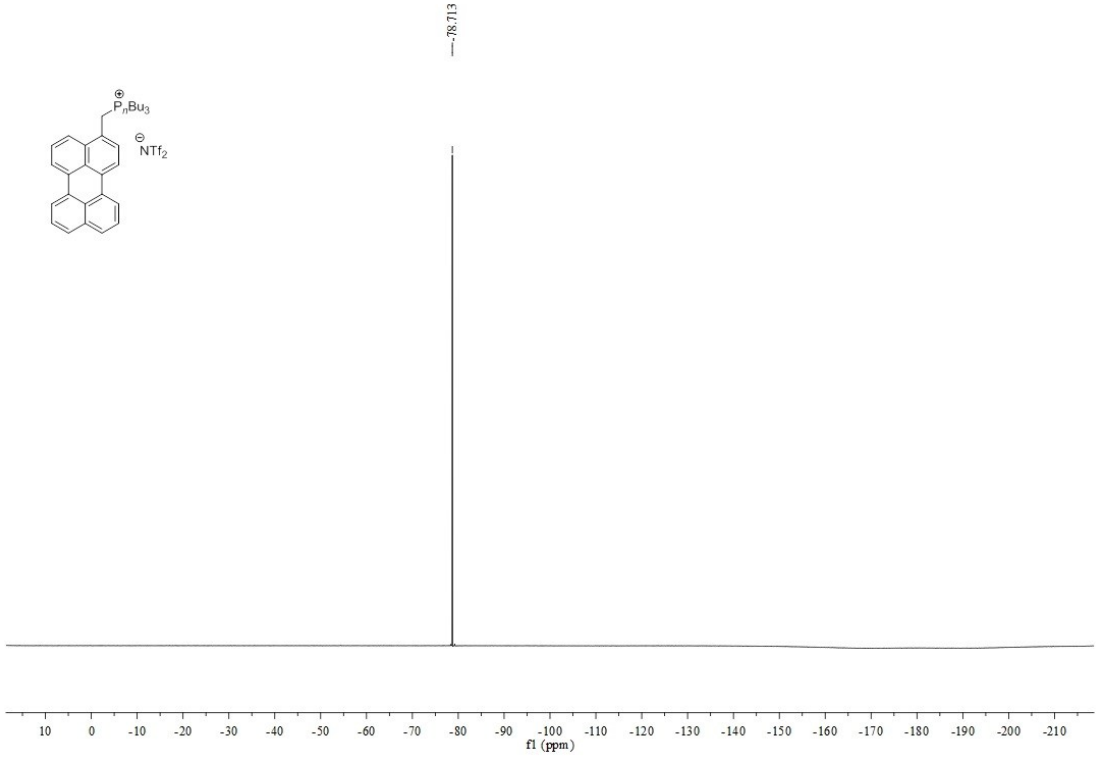
III. Copies of ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra

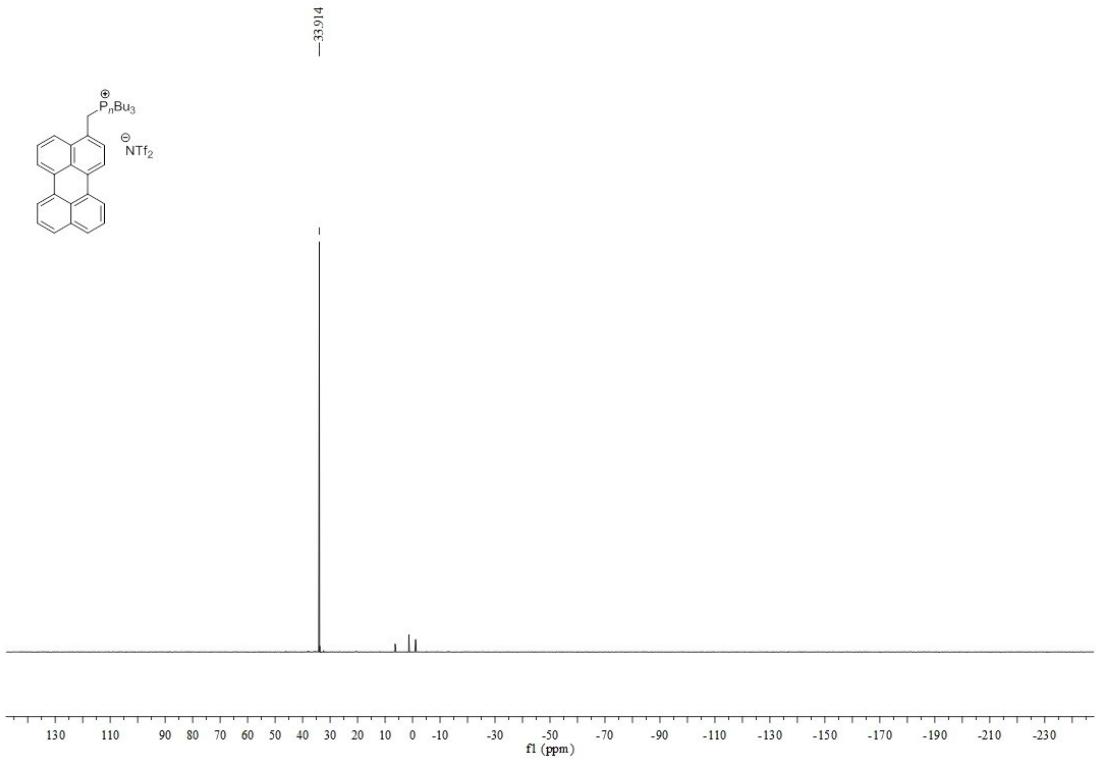


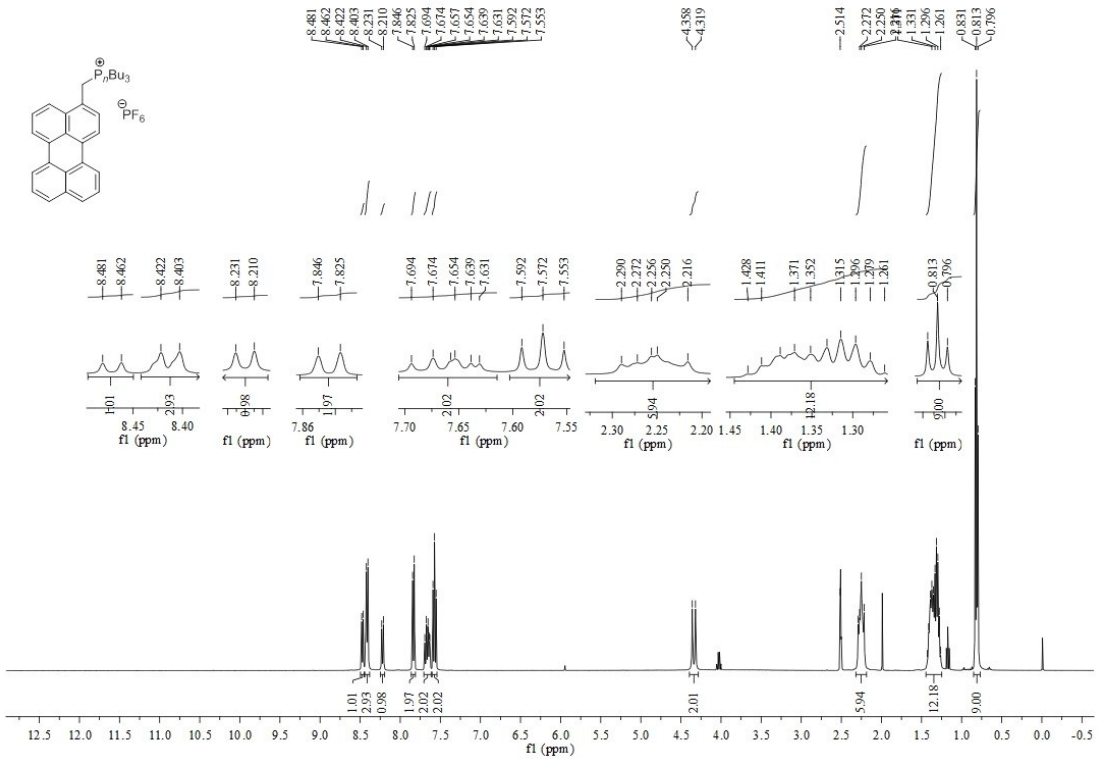

33.882
P_nBu_3
$Br^{\ominus}$
fl (ppm)

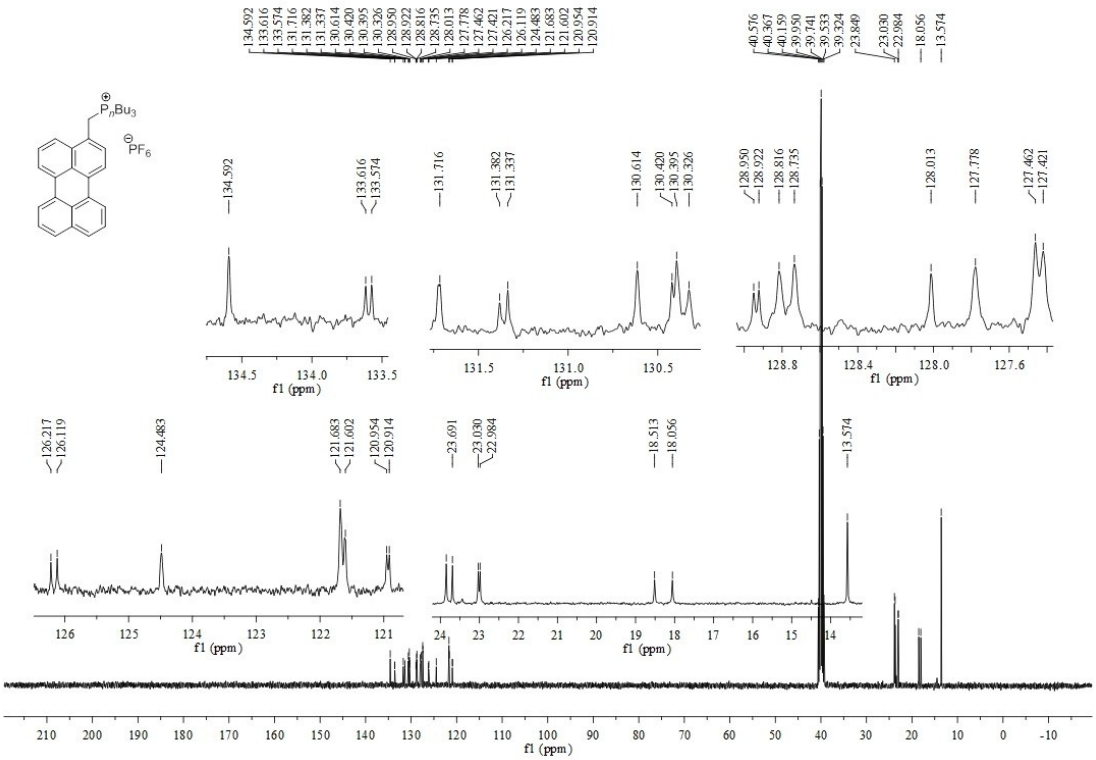

P_nBu_3
$NTf_2^{\ominus}$
fl (ppm)

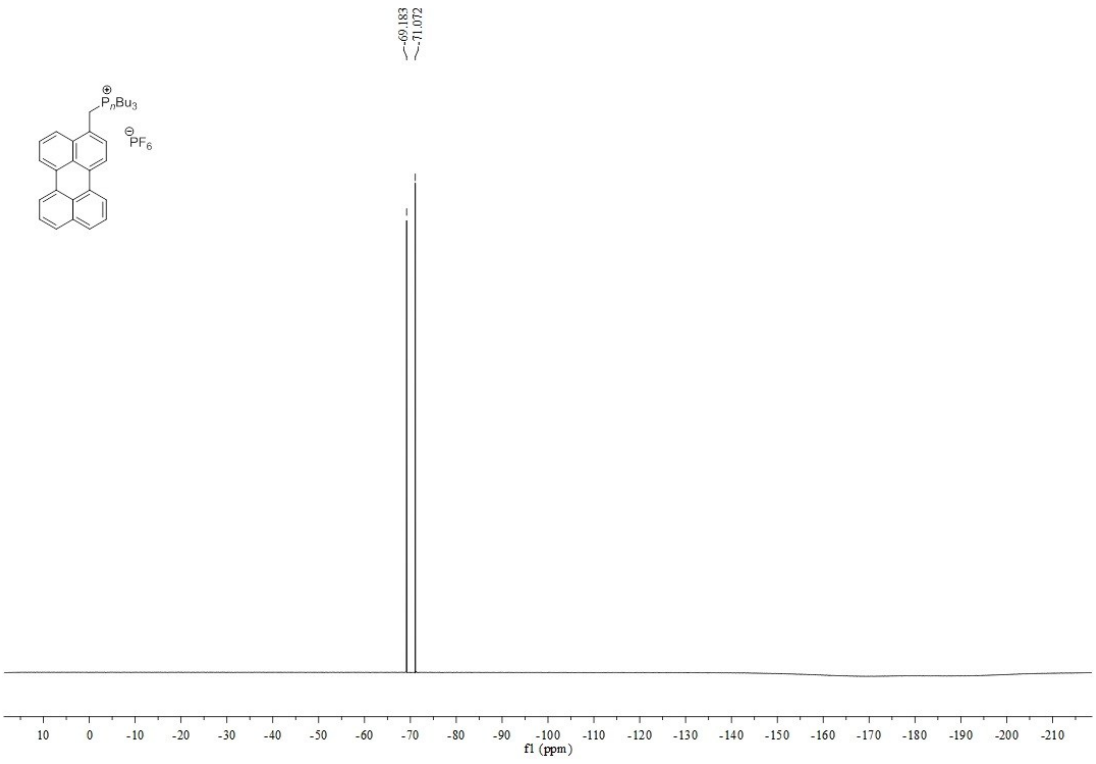

P$_n$Bu$_3$
NTf$_2$
f1 (ppm)

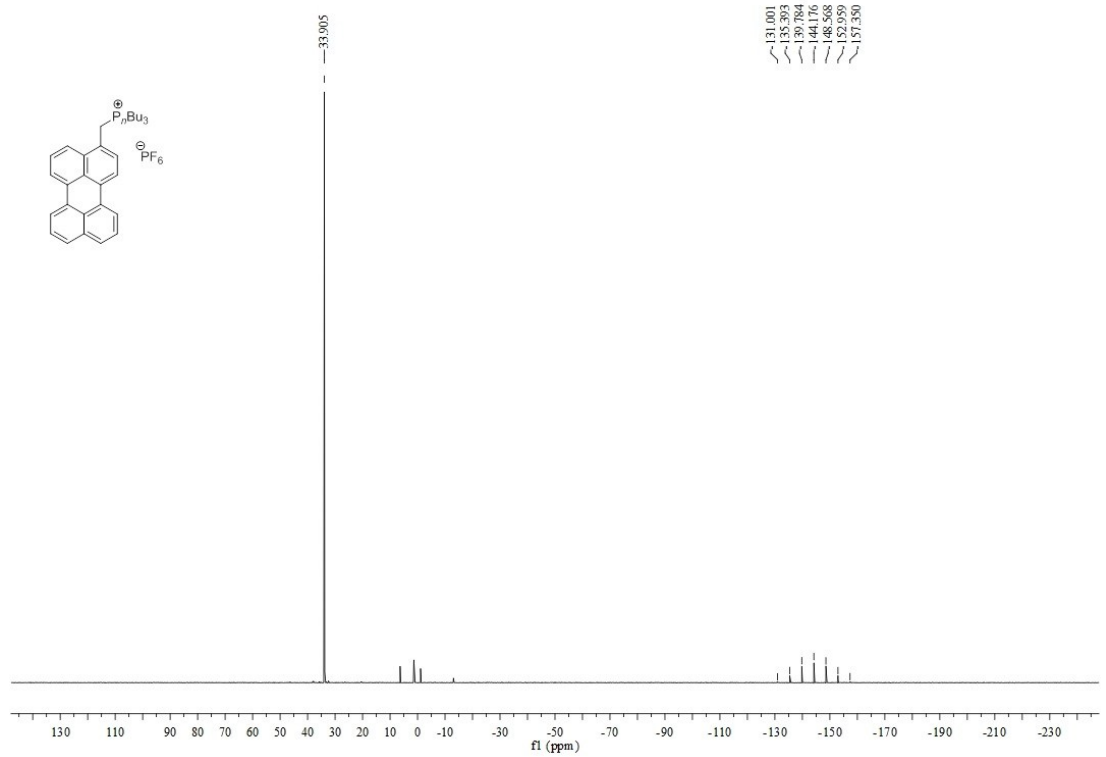

-78.713
P$_n$Bu$_3$
NTf$_2$
f1 (ppm)

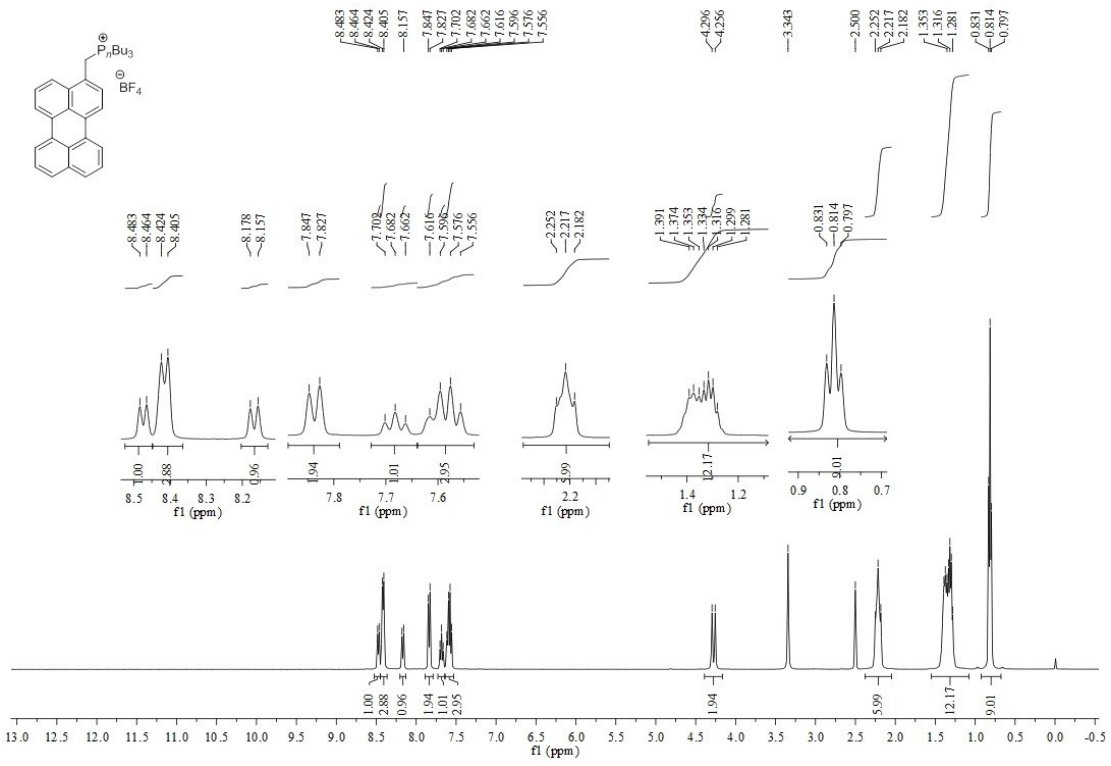

33.914
P_nBu_3
NTf_2
f1 (ppm)

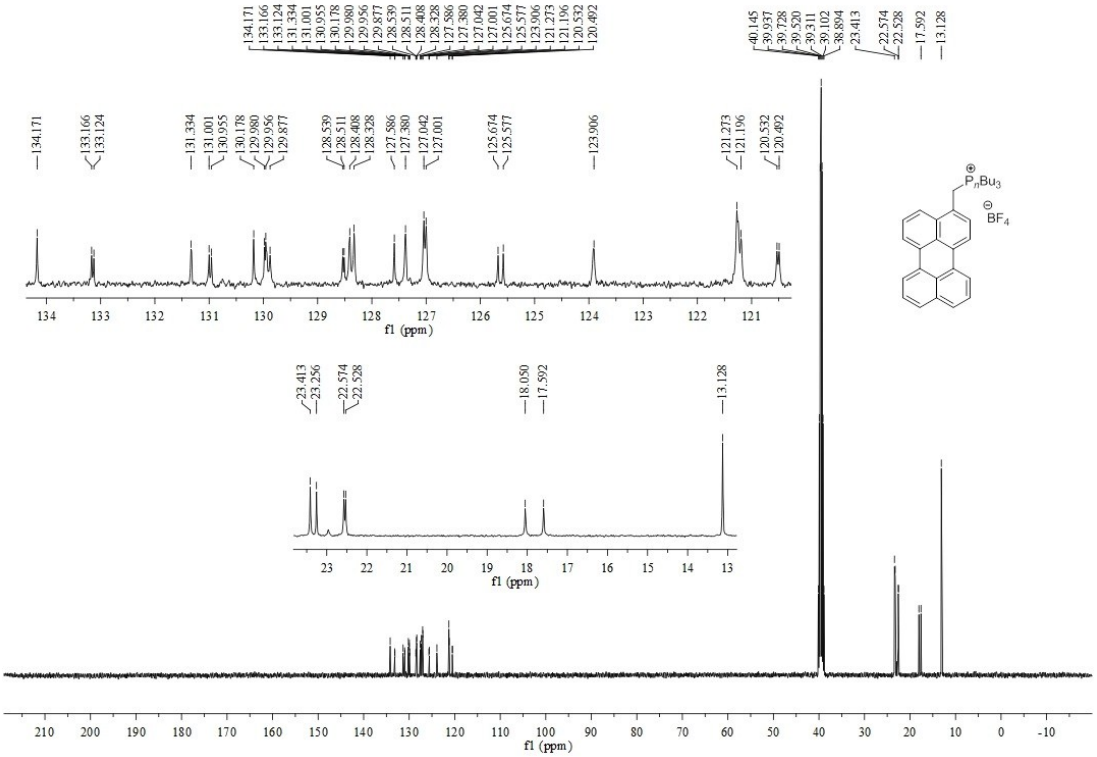

P_nBu_3
PF_6
f1 (ppm)


134.592
133.616
133.574
131.716
131.382
131.337
130.614
130.420
130.395
130.326
128.950
128.922
128.816
128.735
128.013
127.778
127.462
127.421
126.217
126.119
124.483
121.683
121.602
120.954
120.914
40.576
40.367
40.159
39.950
39.741
39.533
39.324
23.849
23.030
22.984
18.056
13.574
f1 (ppm)


-69.183
-71.072
f1 (ppm)


P$_n$Bu$_3$
PF$_6$
33.905
131.001
135.393
139.784
144.176
148.568
152.959
157.350
f1 (ppm)


P$_n$Bu$_3$
BF$_4$
8.483
8.464
8.424
8.405
8.157
7.847
7.827
7.702
7.682
7.662
7.616
7.596
7.576
7.556
4.296
4.256
3.343
2.500
2.252
2.217
2.182
1.353
1.316
1.281
0.831
0.814
0.797
1.00
2.88
0.96
1.94
1.01
2.95
1.94
5.99
12.17
9.01
f1 (ppm)


134.171
133.166
133.124
131.334
131.001
130.955
130.178
129.980
129.956
129.877
128.539
128.511
128.408
128.328
127.586
127.380
127.042
127.001
125.674
125.577
123.906
121.273
121.196
120.532
120.492
40.145
39.937
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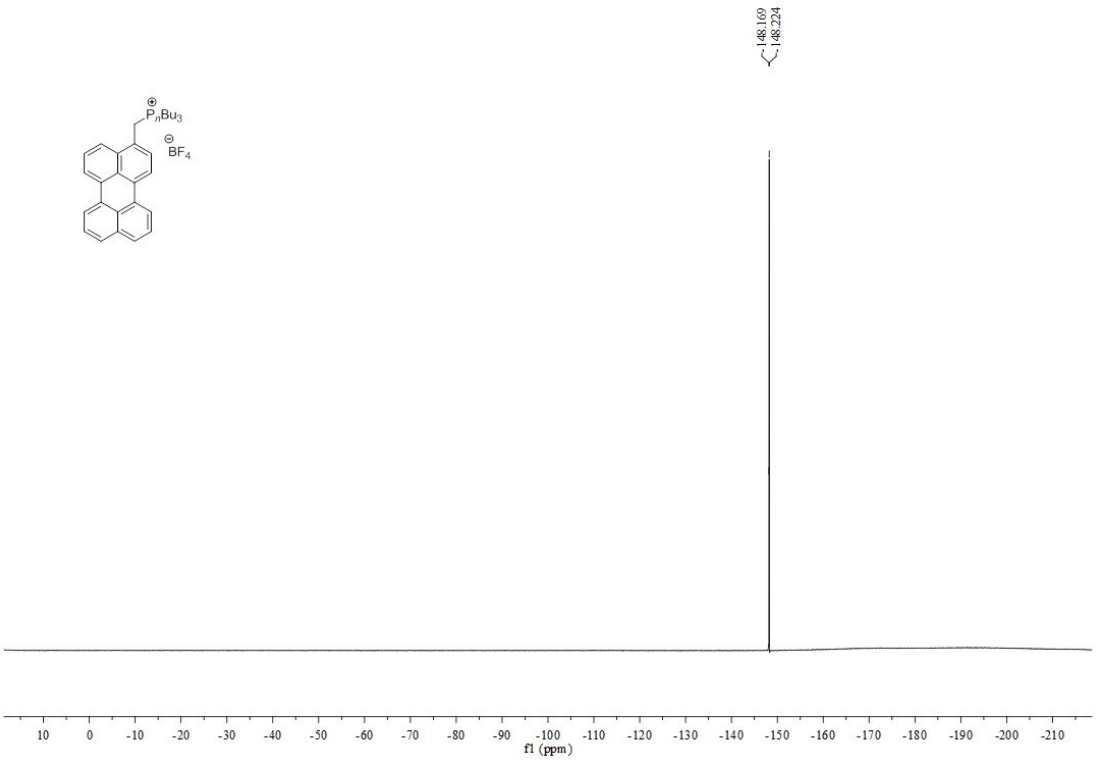
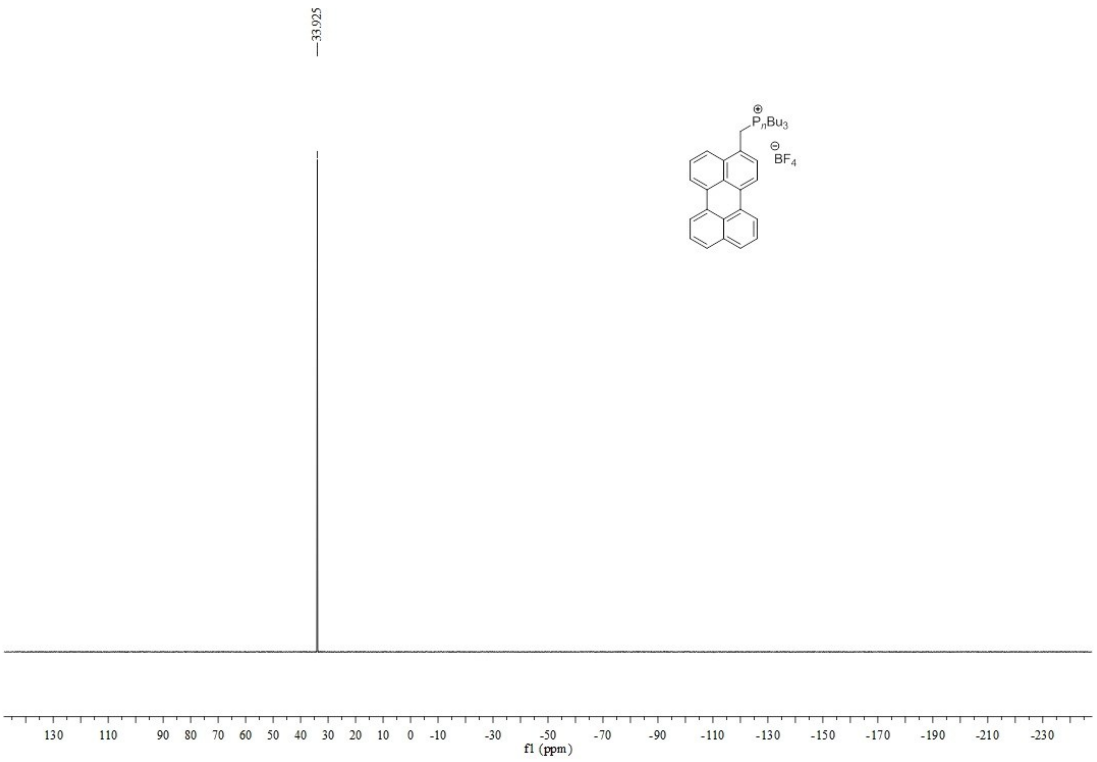
22.574
22.528
17.592
13.128
f1 (ppm)


148.169
148.224
f1 (ppm)


33.925
P_nBu_3
BF_4
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)