Electronic Supplementary Information for:

Molecular Design to Increase the Photosensitivity of Photochromic Phenoxyl-Imidazolyl Radical Complex Derivatives

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CONTENTS

1. ^{1}H NMR Spectra

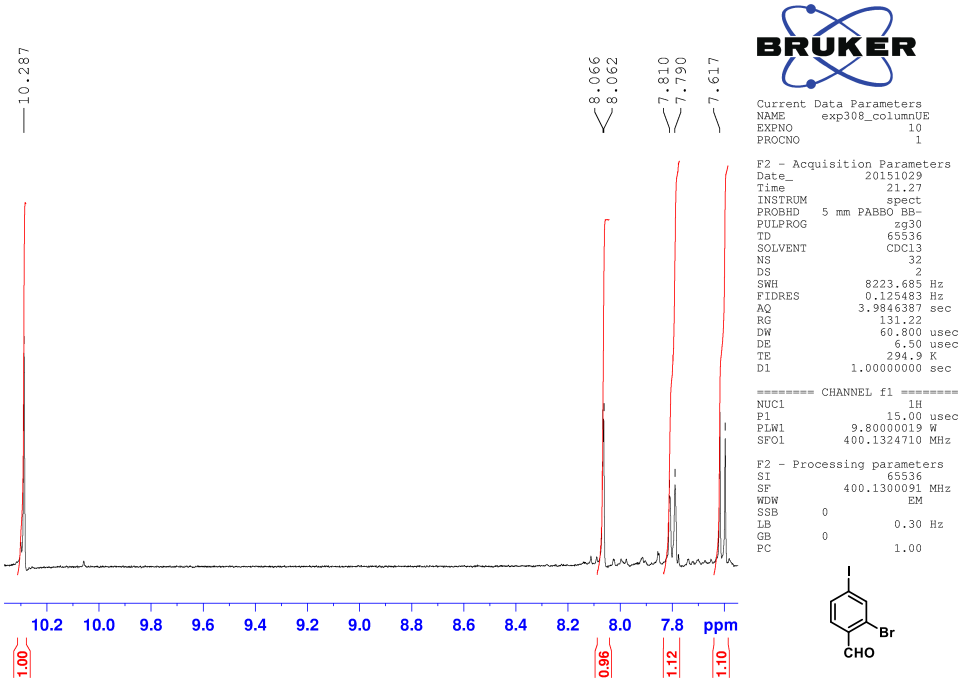

Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$ (* solvent peaks).

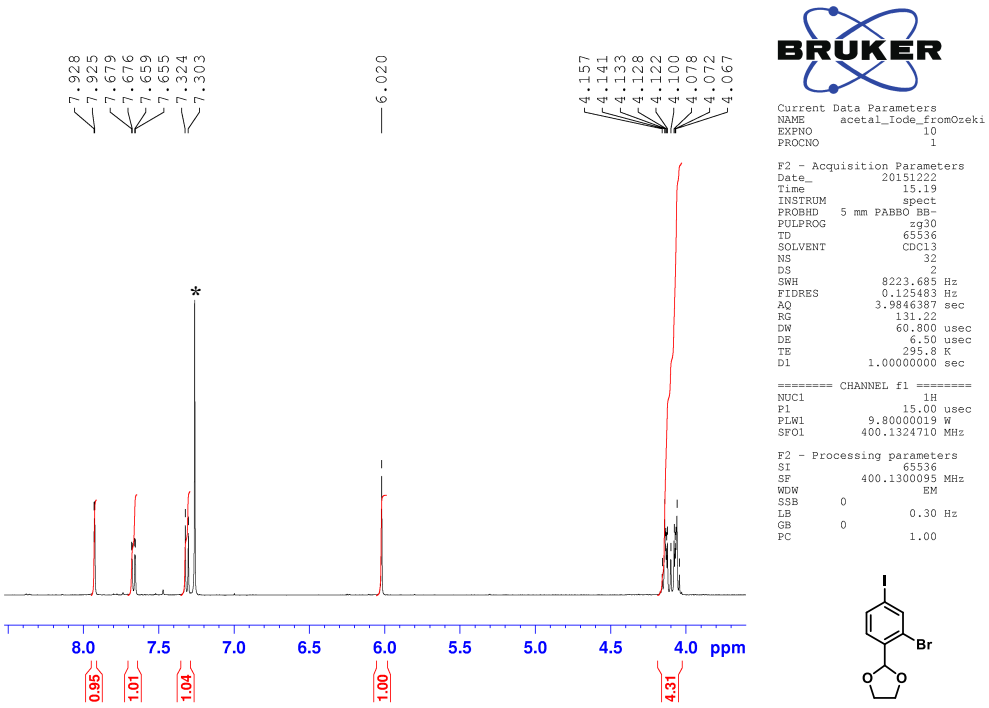

Figure S2. ^{1}H NMR spectrum of **4** in $CDCl_3$ (* solvent peaks).

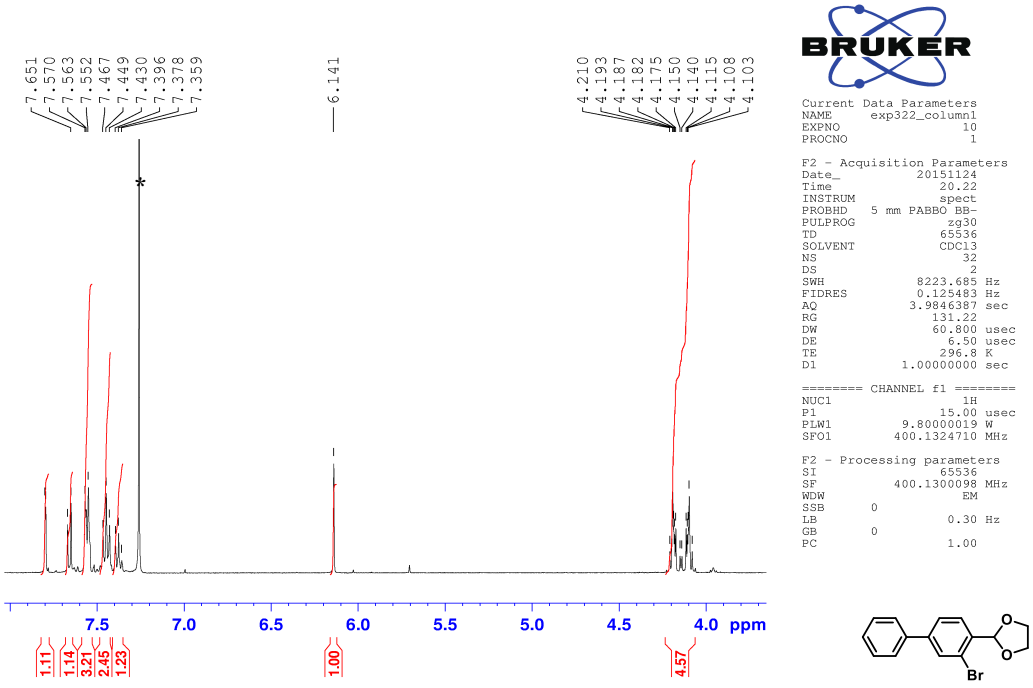

Figure S3. ^{1}H NMR spectrum of **5a** in $CDCl_3$ (* solvent peaks).

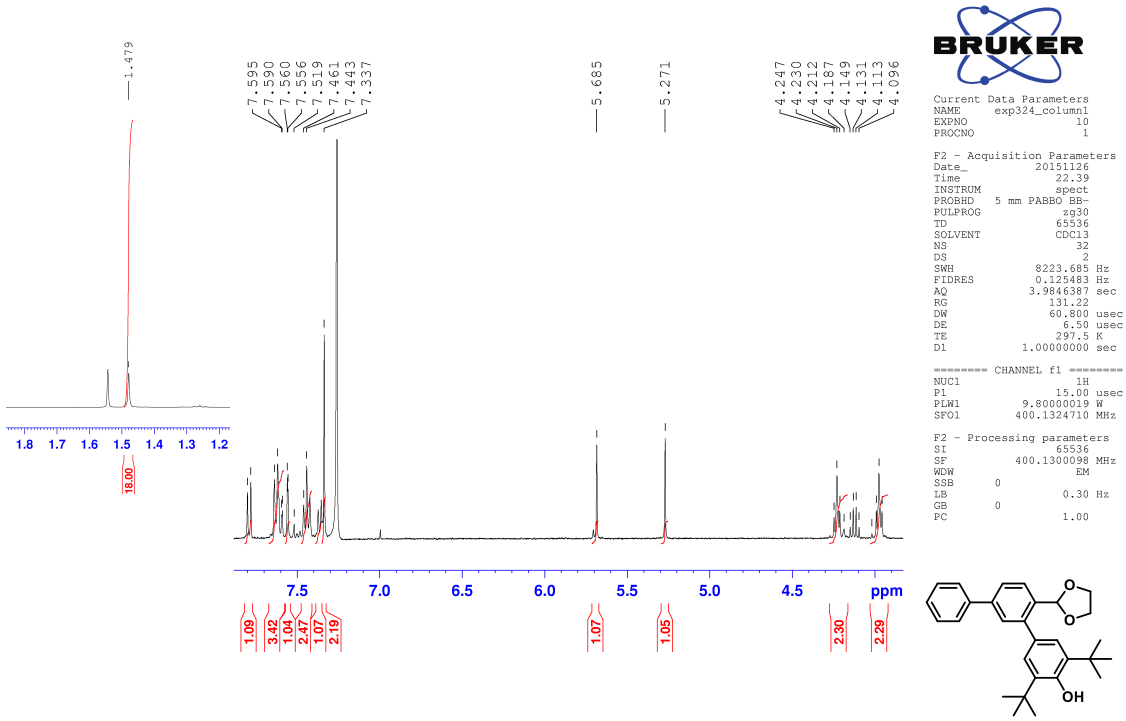

Figure S4. ^{1}H NMR spectrum of **6a** in $CDCl_3$ (* solvent peaks).

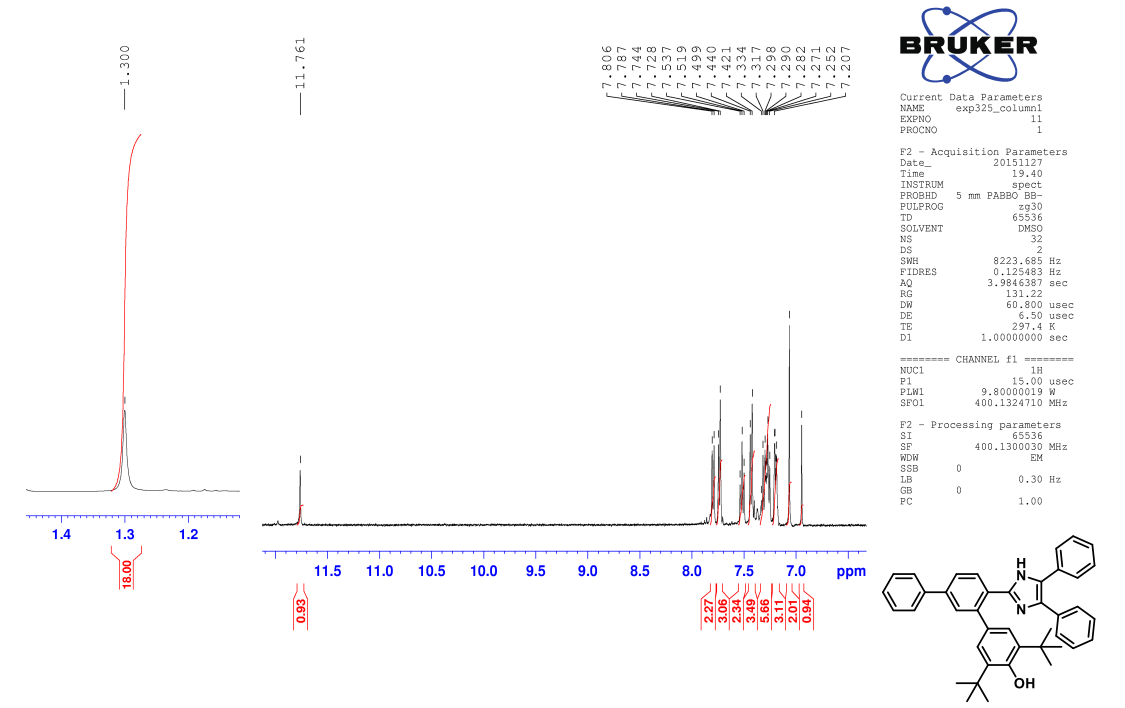

Figure S5. ^{1}H NMR spectrum of **7a** in DMSO-d_6 (* solvent peaks).

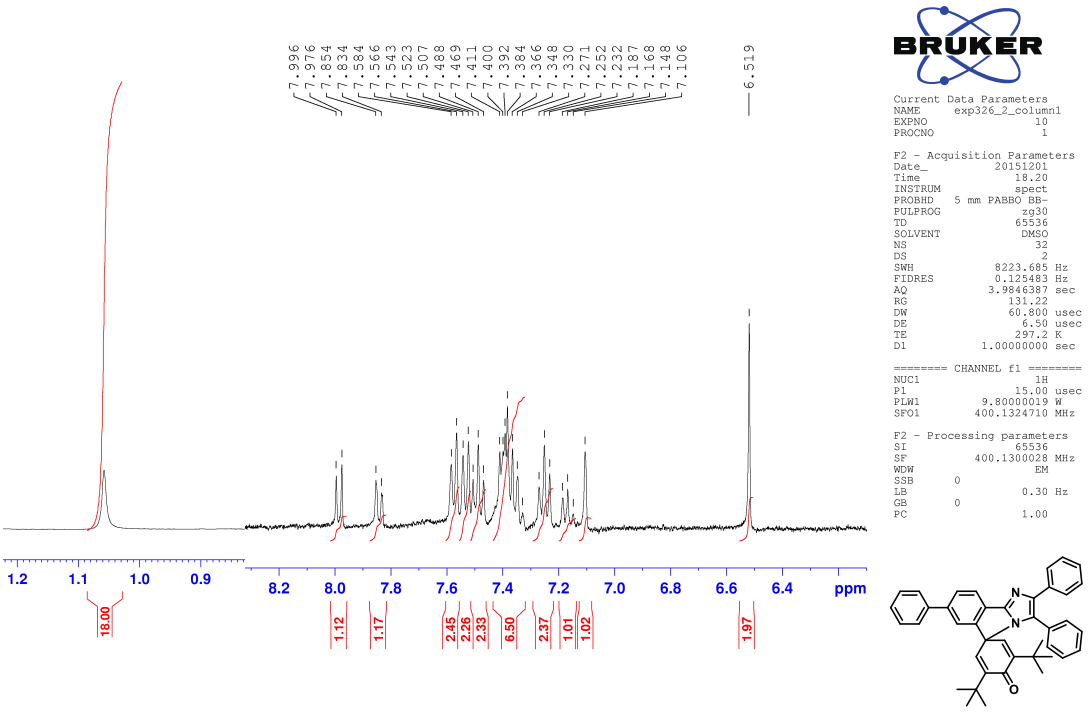

Figure S6. ^{1}H NMR spectrum of **Ph-PIC** in DMSO-d_6 (* solvent peaks).

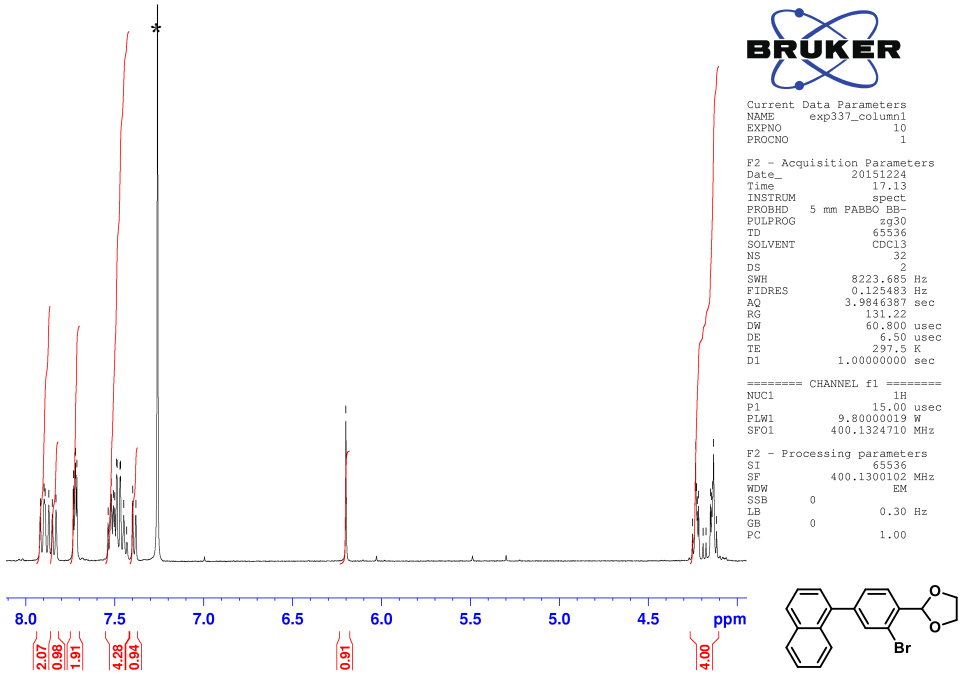

Figure S7. ^{1}H NMR spectrum of **5b** in $CDCl_3$ (* solvent peaks).

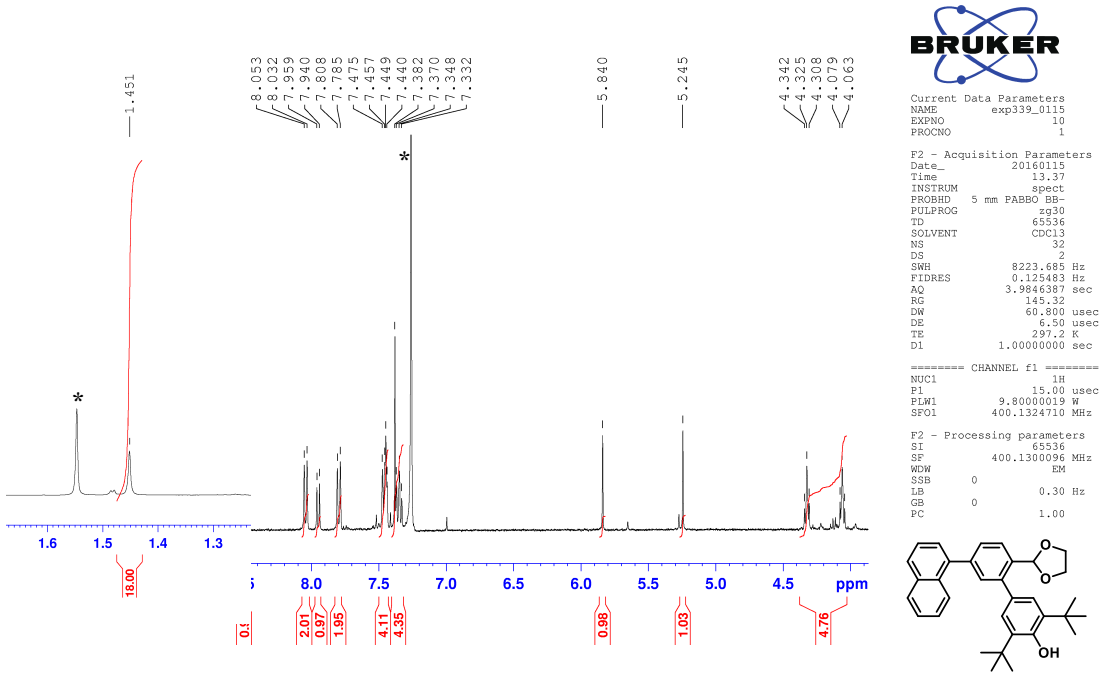

Figure S8. ^{1}H NMR spectrum of **6b** in $CDCl_3$ (* solvent peaks).

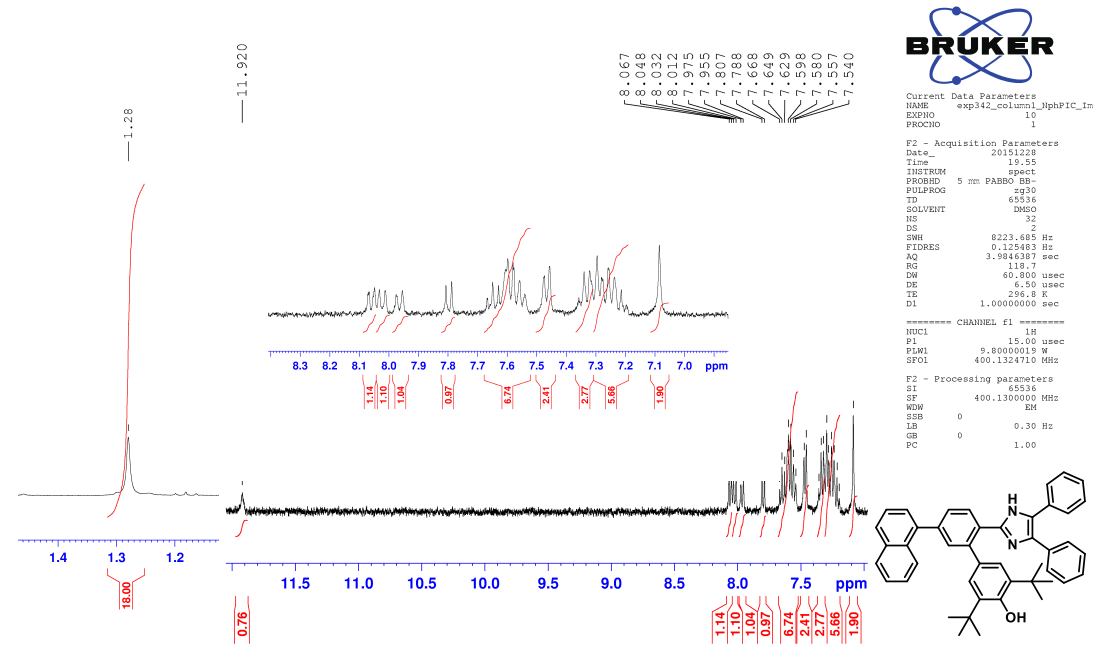

Figure S9. ^{1}H NMR spectrum of **7b** in DMSO-d_6 (* solvent peaks).

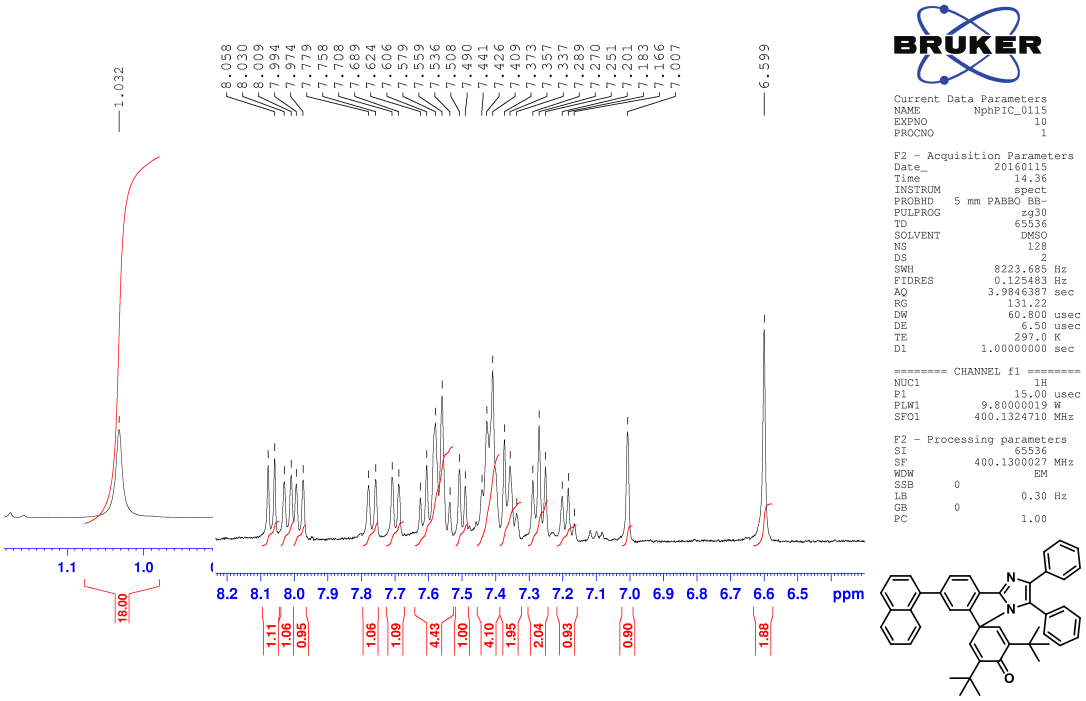

Figure S10. ^{1}H NMR spectrum of **Np-PIC** in DMSO-d_6 (* solvent peaks).

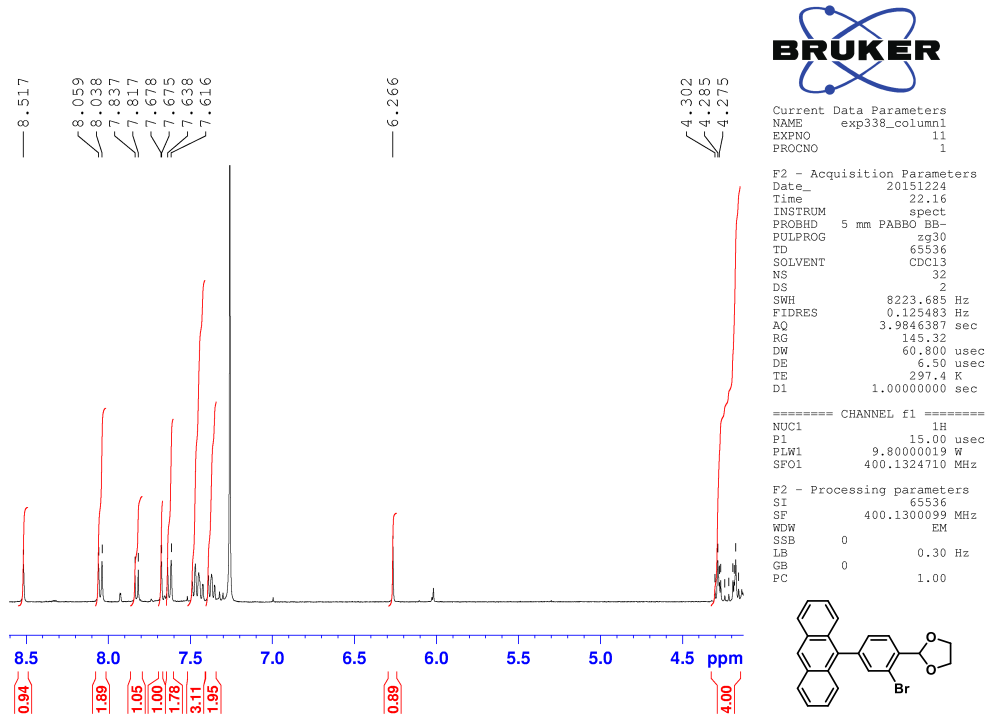

Figure S11. ^{1}H NMR spectrum of **5c** in $CDCl_3$ (* solvent peaks).

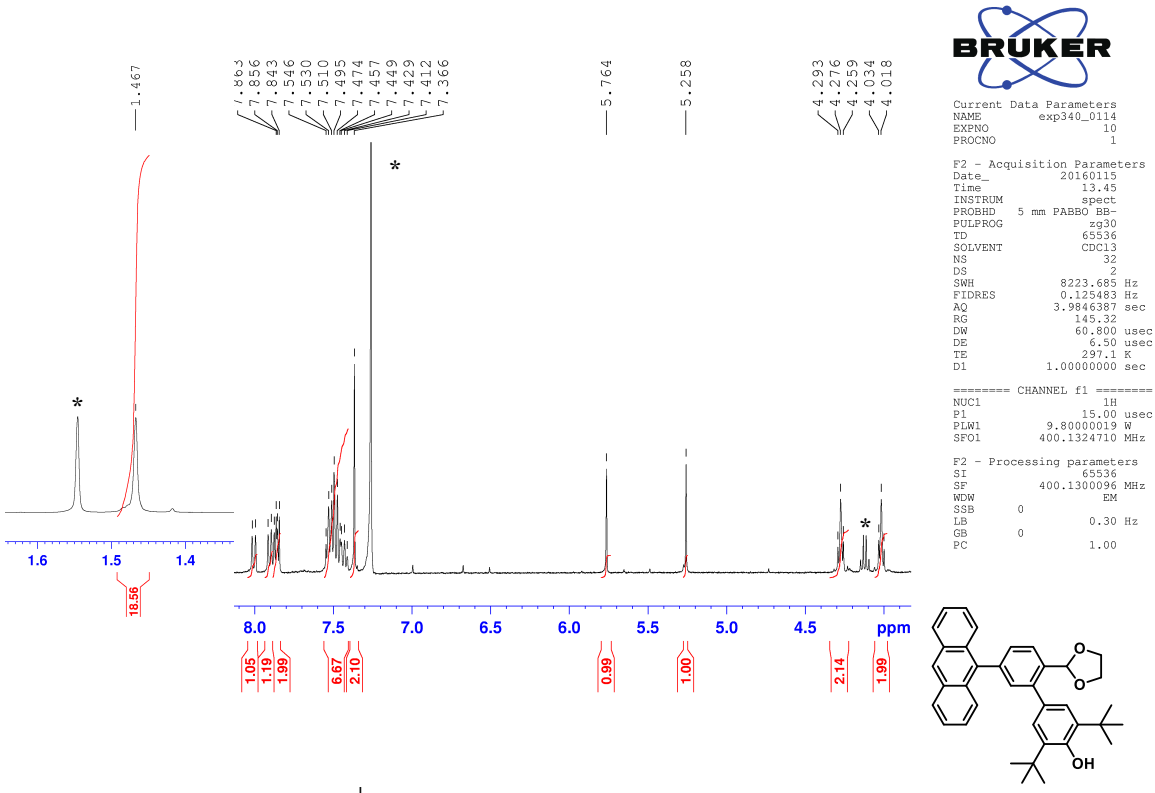

Figure S12. ^{1}H NMR spectrum of **6c** in $CDCl_3$ (* solvent peaks).

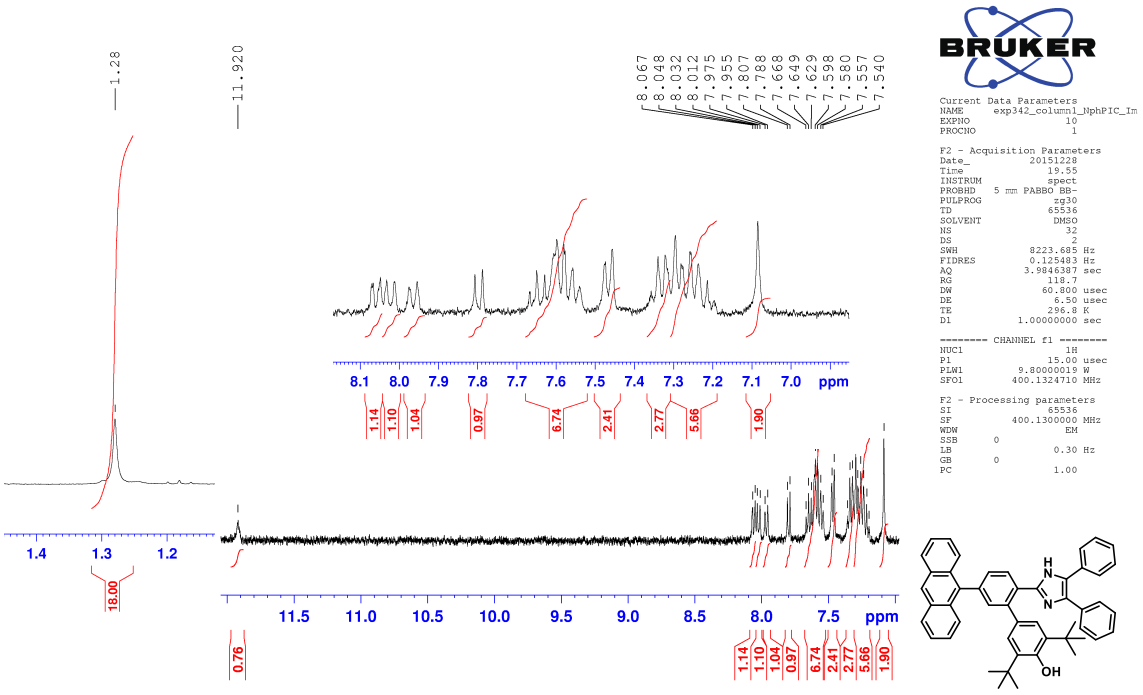

Figure S13. ^{1}H NMR spectrum of **7c** in DMSO-d_6 (* solvent peaks).

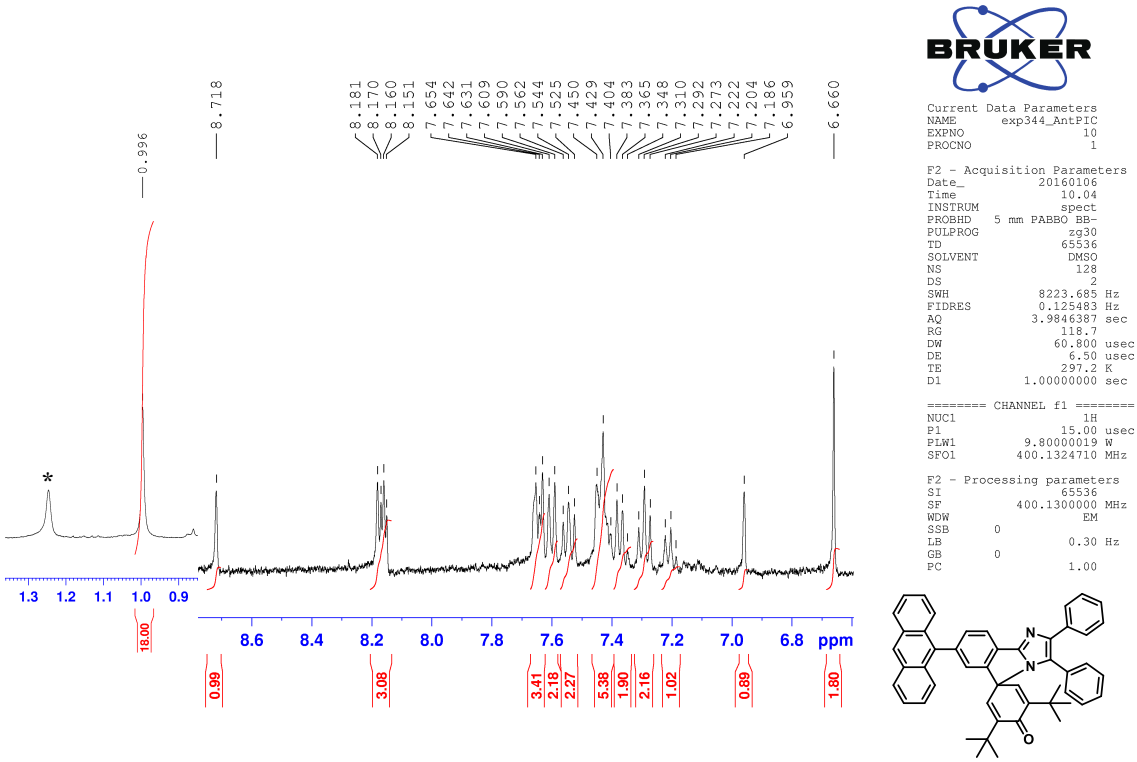

Figure S14. ^{1}H NMR spectrum of **An-PIC** in DMSO-d_6 (* solvent peaks).

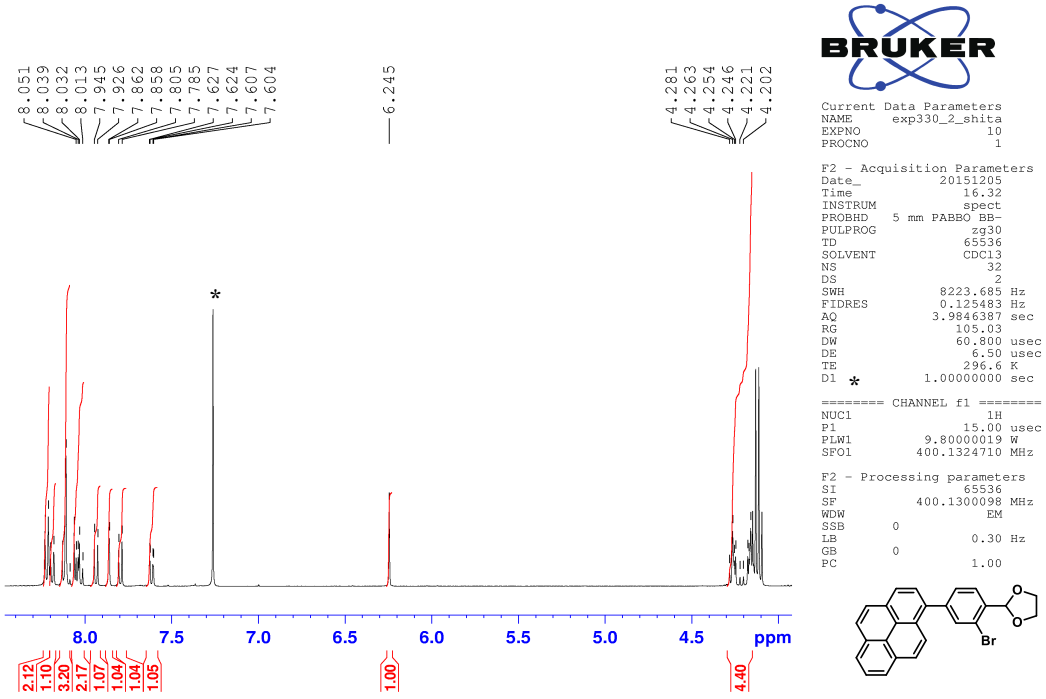

Figure S15. ^{1}H NMR spectrum of **5d** in $CDCl_3$ (* solvent peaks).

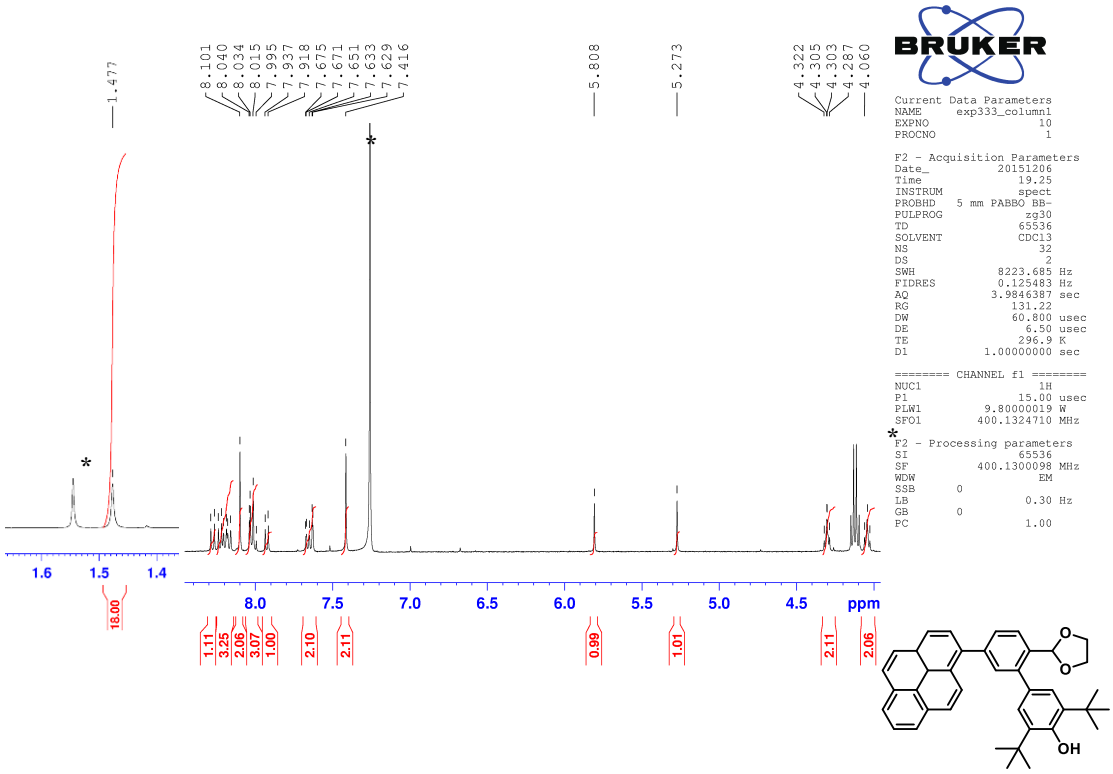

Figure S16. ^{1}H NMR spectrum of compound **6d** in $CDCl_3$ (* solvent peaks).

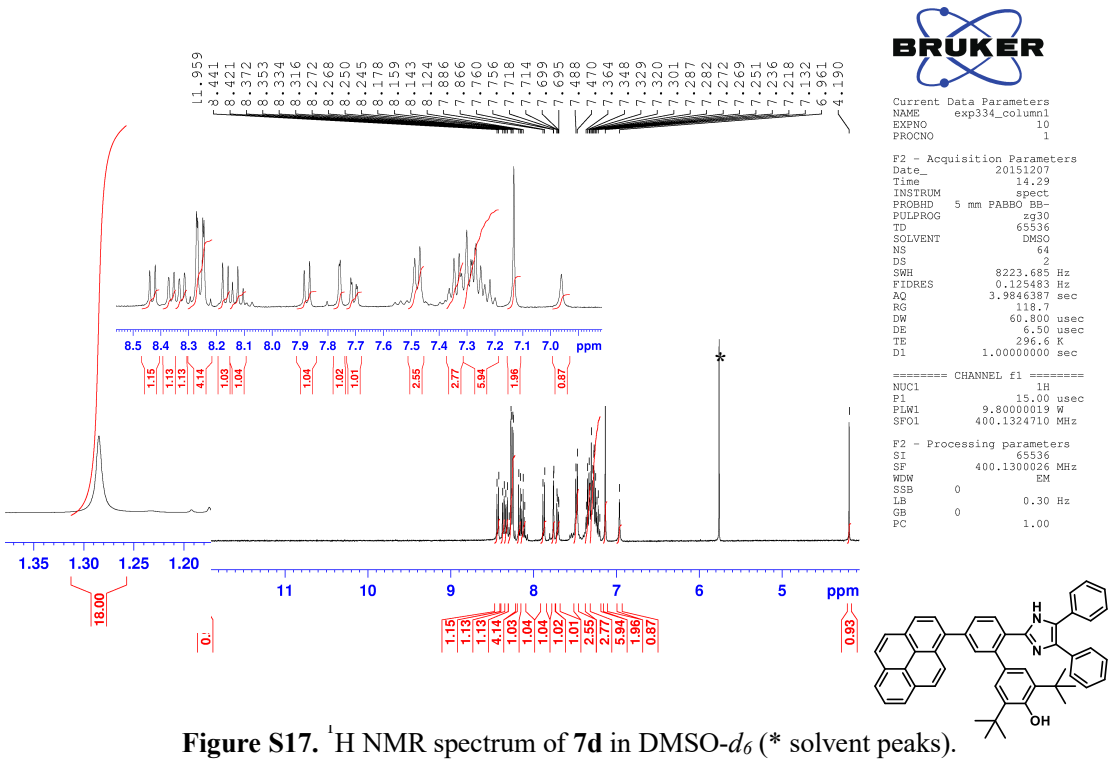

Figure S17. ^{1}H NMR spectrum of **7d** in DMSO-d_6 (* solvent peaks).

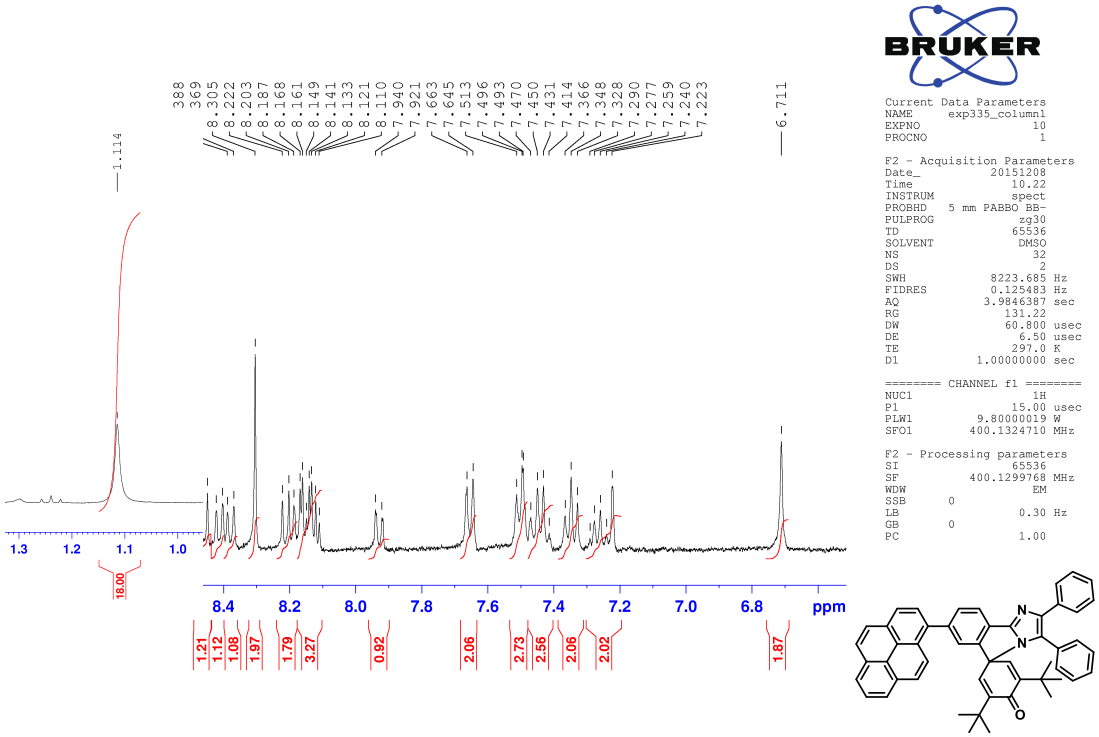

Figure S18. ^{1}H NMR spectrum of compound **Py-PIC** in DMSO-d_6 (* solvent peaks).

2. HR-ESI-TOF-MS-Spectra

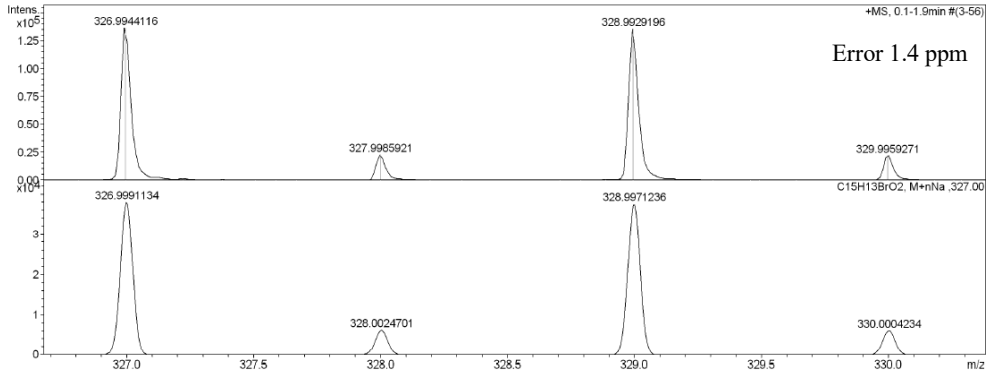

Figure S19. HR-ESI-TOF-MS of **5a**.

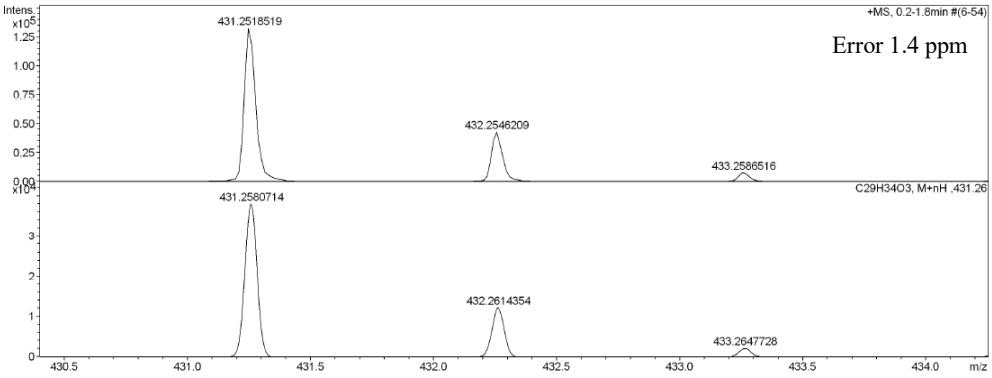

Figure S20. HR-ESI-TOF-MS of **6a**.

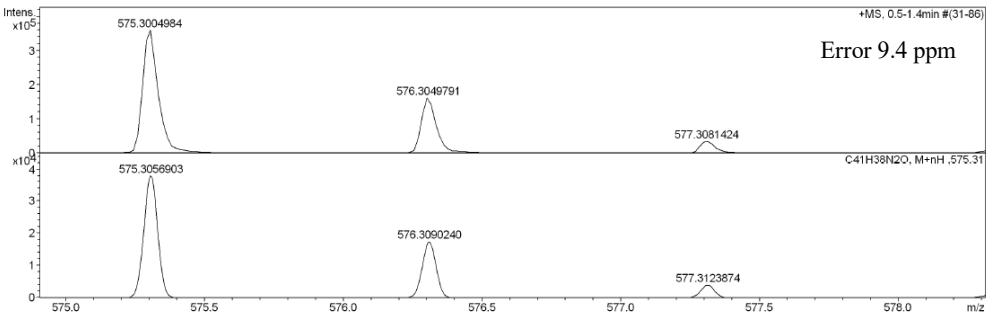

Figure S21. HR-ESI-TOF-MS of **Ph-PIC**.

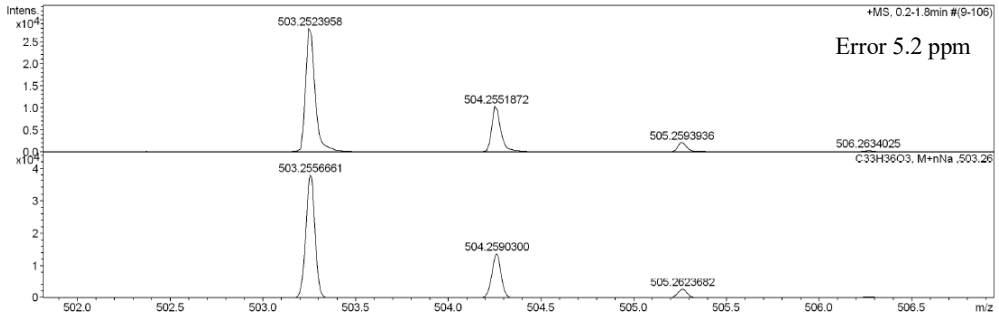

Figure S22. HR-ESI-TOF-MS of **6b**.

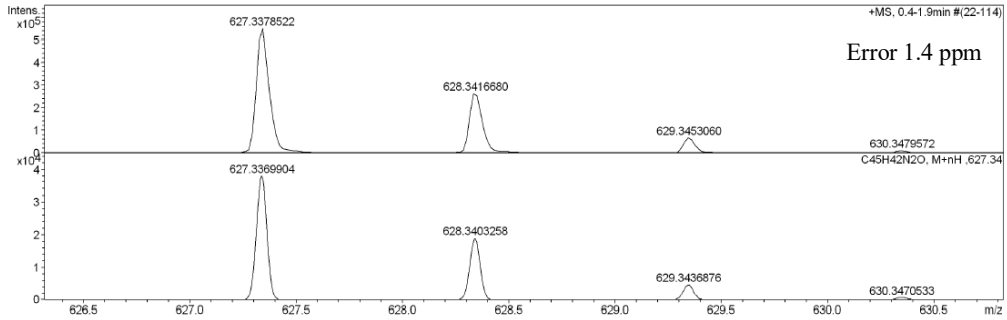

Figure S23. HR-ESI-TOF-MS of **7b**.

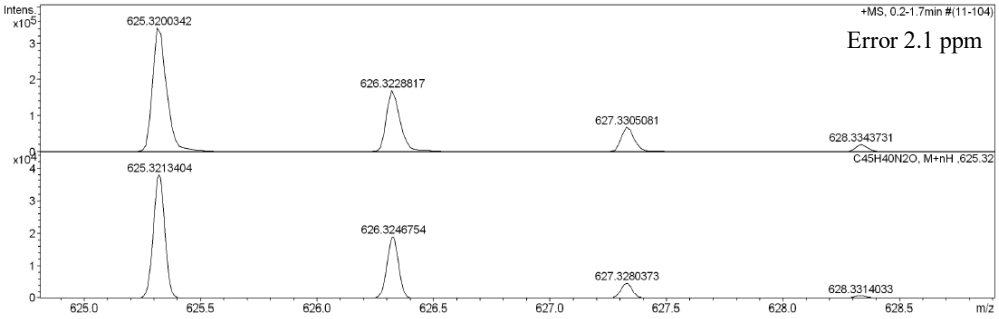

Figure S24. HR-ESI-TOF-MS of **Np-PIC**.

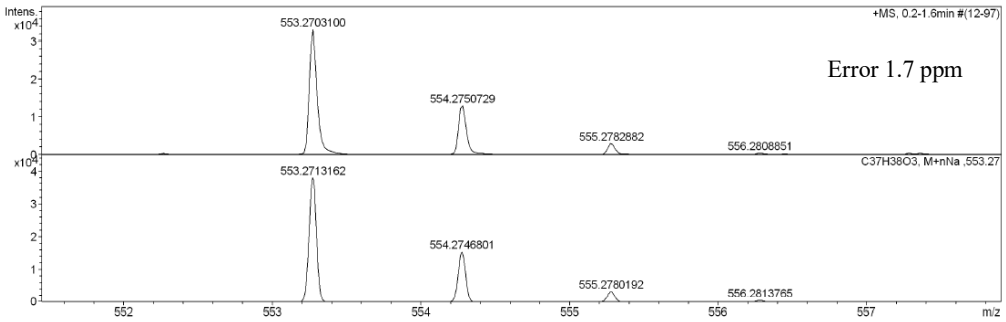

Figure S25. HR-ESI-TOF-MS of **6c**.

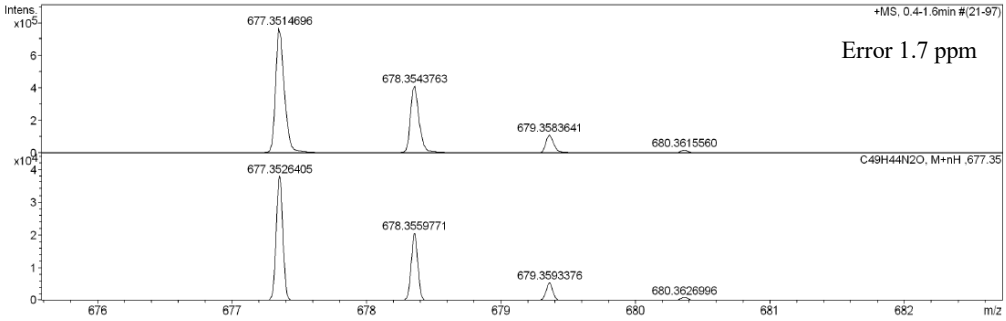

Figure S26. HR-ESI-TOF-MS of **7c**.

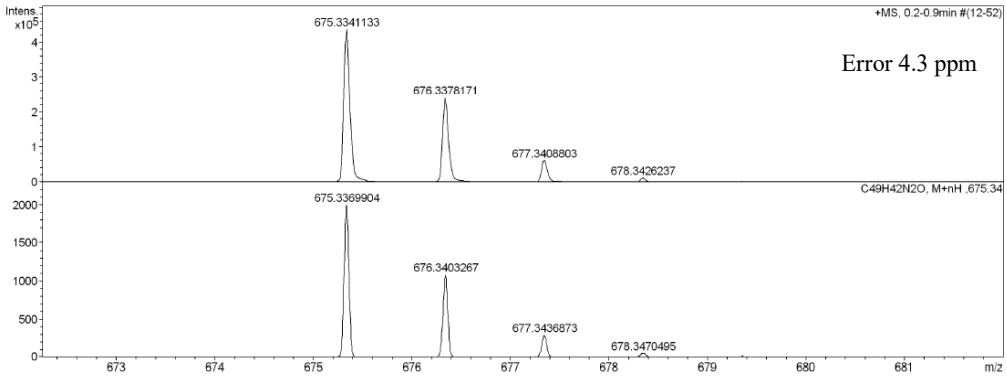

Figure S27. HR-ESI-TOF-MS of **An-PIC**.

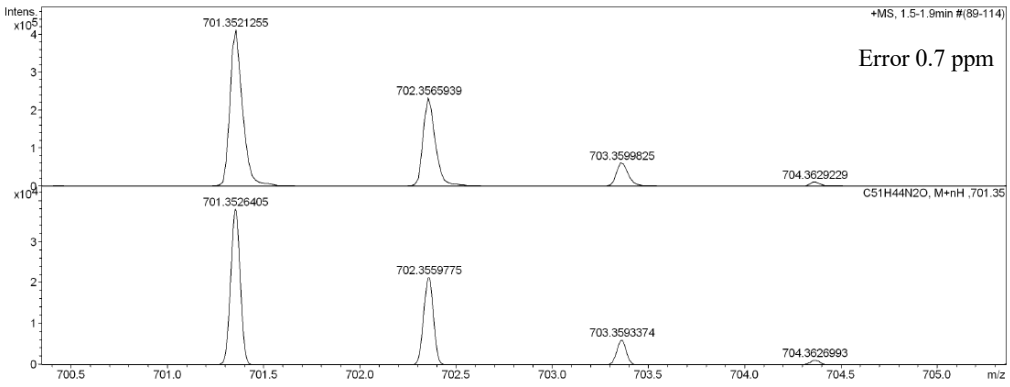

Figure S28. HR-ESI-TOF-MS of **7d**.

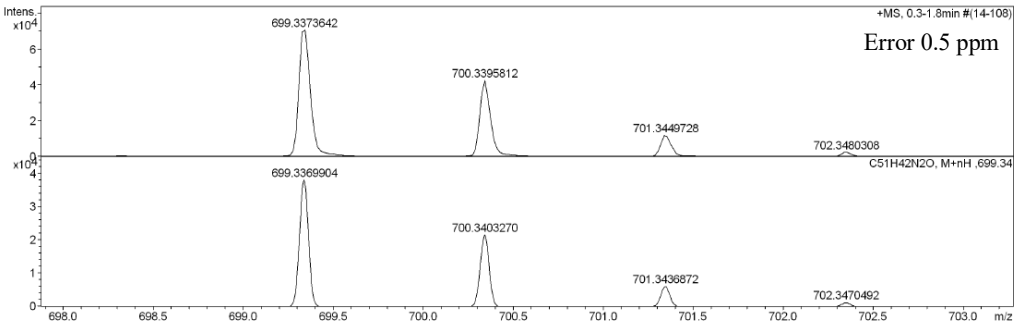

Figure S29. HR-ESI-TOF-MS of **Py-PIC**.

3. HPLC Chromatogram

HPLC analysis was performed by using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5μm particle) from Kanto Chemical Co., Inc. The mobile phase was CH_3CN (detection wavelength; 254, 300 and 355 nm). The HPLC analytical system consists of a pump unit (PU-2080 plus, JASCO), a photodiode array detector (MD-2018, JASCO), and a control unit (LCNetII/ADC, JASCO).

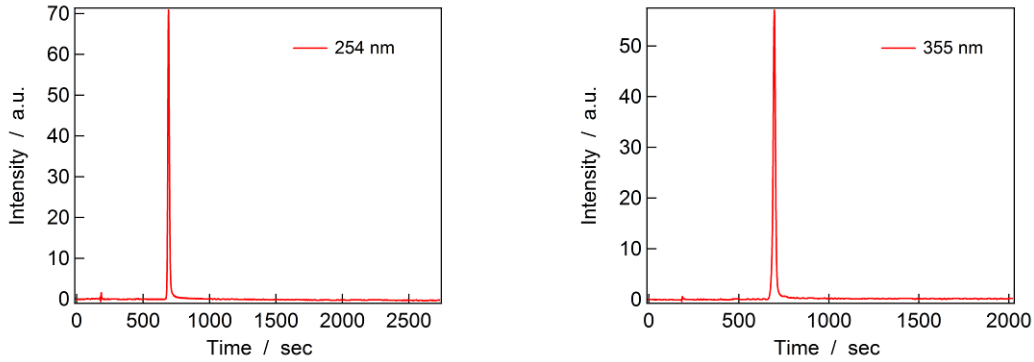

Figure S30. HPLC charts of **Ph-PIC** (inject: 2μL, $\lambda_{abs.}$ = 254 nm and 355 nm, eluent: CH_3CN).

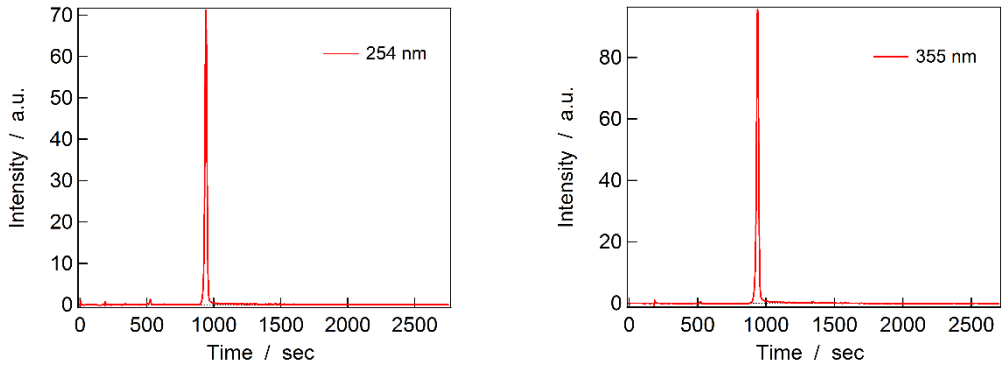

Figure S31. HPLC charts of **Np-PIC** (inject: 2μL, $\lambda_{abs.}$ = 254 nm and 355 nm, eluent: CH_3CN).

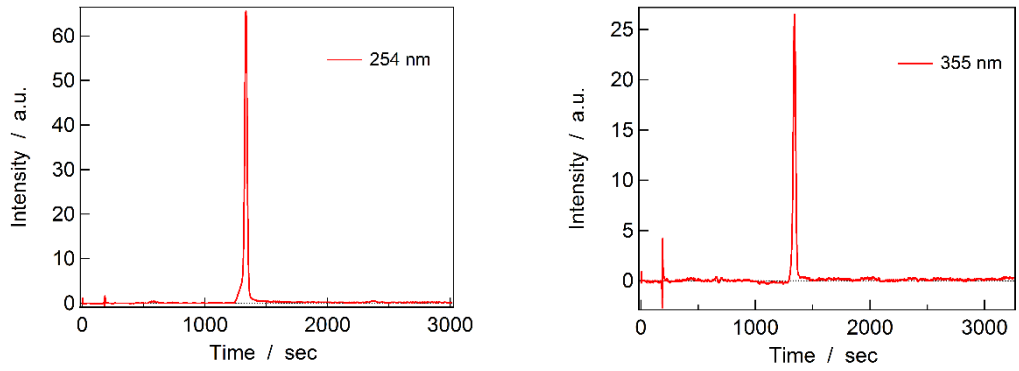

Figure S32. HPLC charts of **An-PIC** (inject: 2μL, $\lambda_{abs.}$ = 254 nm and 355 nm, eluent: CH_3CN).

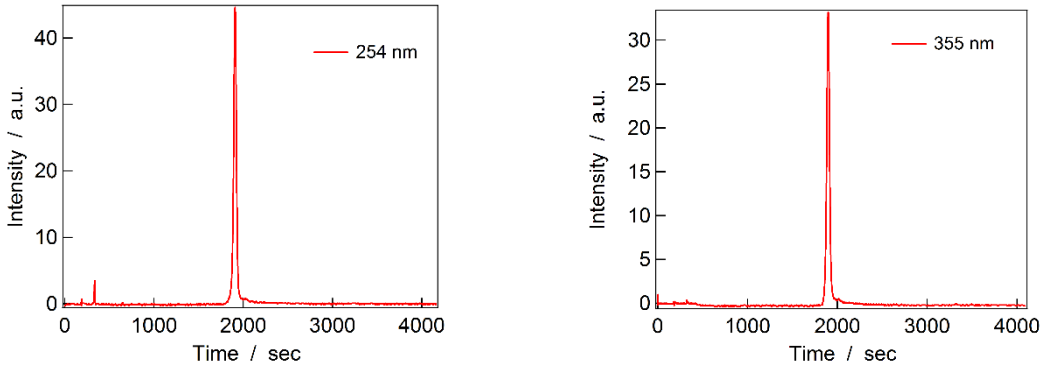

Figure S33. HPLC charts of **Py-PIC** (inject: 2μL, $\lambda_{abs.}$ = 254 nm and 355 nm, eluent: CH_3CN).

4. Transient Vis-NIR Absorption Spectra

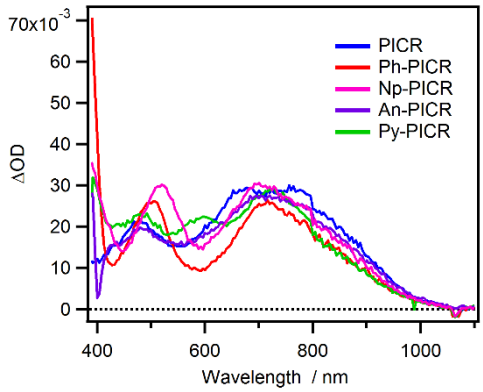

Figure S34. The profile of the transient absorption spectra of **PICR**, **Ph-PICR**, **Np-PICR**, **An-PICR** and **Py-PICR** in toluene at 20 ns after 355 nm excitation, observed at 700 nm (183 K, power: 4.2 mJ).

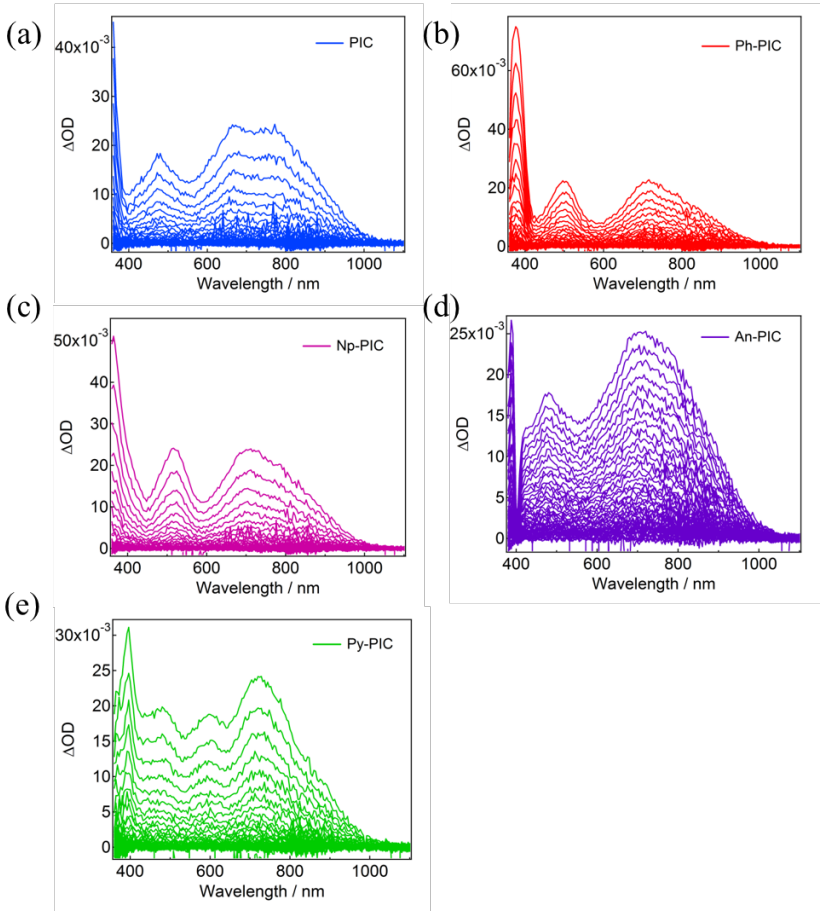

Figure S35. Transient vis-NIR spectra of (a) **PIC**, (b) **Ph-PIC**, (c) **Np-PIC**, (d) **An-PIC** and (e) **Py-PIC** in toluene. (excitation wavelength: 355 nm, Temp.: 183 K, power: 4.2 mJ, time interval: 4.0 ns).

5. TD-DFT Calculations for the UV–vis Absorption Spectra

All calculations were carried out using the Gaussian 09 program (Revision D.01).[S1] The molecular structures were fully optimized at the UM052X/6-31G(d) level of theory, and analytical second derivative was computed using vibrational analysis to confirm each stationary point to be a minimum. TDDFT calculations were performed at the UMPW1PW91/6-31+G(d,p) level of the theory for the optimized structures.

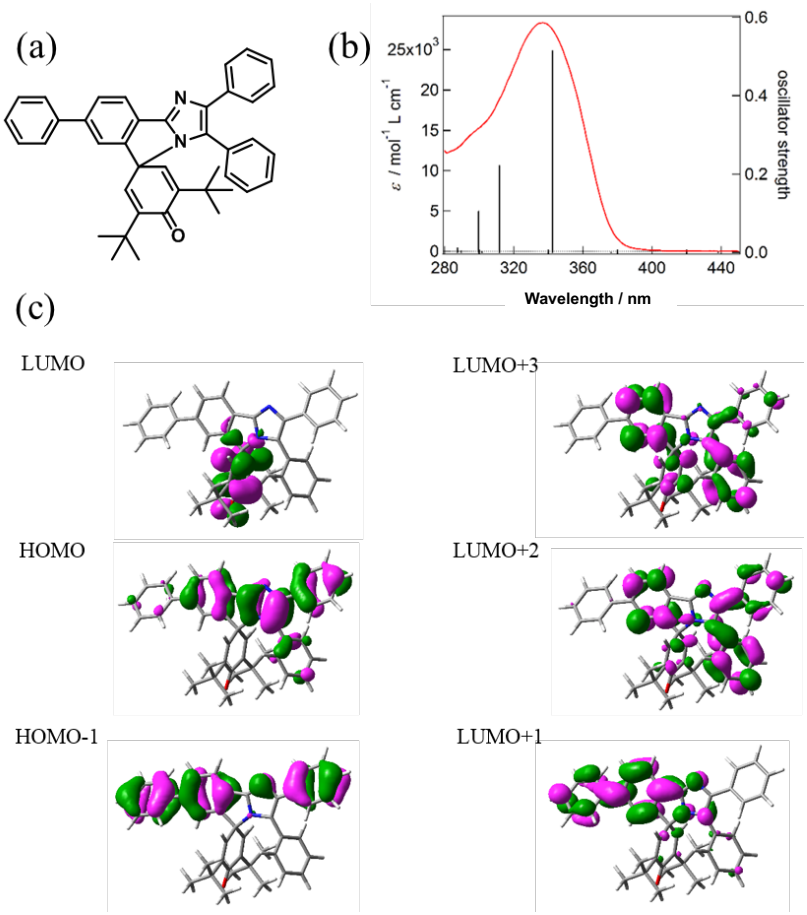

Figure S36. (a) Molecular structure of compound **Ph-PIC**; (b) UV–vis absorption spectrum of **Ph-PIC**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **Ph-PIC**.

Table S1. Standard Orientation of the Optimized Geometry for **Ph-PIC**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.4579610	-2.2642060	-0.0014800
2	C	2.8417340	-3.5175660	0.1340690
3	C	1.4629050	-3.6485610	0.2632010
4	C	0.6900550	-2.4947500	0.2593690
5	C	1.2966780	-1.2407040	0.1229960

6	C	2.6643770	-1.1077390	-0.0027050
7	C	4.9301950	-2.1603330	-0.1419040
8	C	-0.7468820	-2.2697770	0.3405390
9	C	0.2463990	-0.1159160	0.1519010
10	C	0.2023200	0.6373120	-1.1396730
11	C	0.5155320	1.9317140	-1.2646120
12	C	0.9643420	2.6815490	-0.0466180
13	N	-1.8553740	-2.9630290	0.3356800
14	C	-2.8592870	-2.0189570	0.2712800
15	C	5.6359280	-1.1354800	0.4970580
16	C	7.0156970	-1.0344850	0.3628490
17	C	7.7127970	-1.9575630	-0.4115100
18	C	7.0203170	-2.9815840	-1.0513560
19	C	5.6403080	-3.0817000	-0.9184800
20	C	0.8728390	2.0203810	1.2975610
21	C	0.5051410	0.7353810	1.3557980
22	C	0.4301280	2.6752090	-2.5953180
23	O	1.3929540	3.8213800	-0.1438250
24	C	1.1938860	2.8441900	2.5430000
25	C	2.6643090	3.2984190	2.5085220
26	C	0.9873140	2.0225080	3.8198610
27	C	0.2647060	4.0684470	2.6190900
28	C	1.8291260	3.1369070	-3.0394360
29	C	-0.5101470	3.8860360	-2.4533760
30	C	-0.1442650	1.7729600	-3.6926340
31	C	-2.3302450	-0.7321510	0.2245790
32	N	-0.9703490	-0.9252100	0.3038040
33	C	-4.2707730	-2.4339280	0.2562170
34	C	-2.9292270	0.5943570	-0.0024450
35	C	-2.6894060	1.6607840	0.8687810
36	C	-3.2170210	2.9198170	0.6009030
37	C	-4.0055860	3.1216730	-0.5282590
38	C	-5.2986900	-1.5875870	0.6855810
39	C	-6.6212560	-2.0150220	0.6515100
40	C	-6.9357360	-3.2938790	0.2006260
41	C	-5.9151150	-4.1473450	-0.2108940
42	C	-4.5927600	-3.7222810	-0.1831540
43	C	-4.2635700	2.0589940	-1.3920380
44	C	-3.7245810	0.8039730	-1.1345710
45	H	3.4638150	-4.4032510	0.1630080
46	H	0.9999550	-4.6200330	0.3727050
47	H	3.1147650	-0.1299790	-0.1312760
48	H	-0.1104660	0.0412160	-1.9871000
49	H	5.1011440	-0.4305350	1.1220840
50	H	7.5473240	-0.2393880	0.8701630
51	H	8.7874500	-1.8790540	-0.5160420
52	H	7.5538980	-3.6981730	-1.6628450
53	H	5.1026230	-3.8628150	-1.4418120

54	H	0.4221540	0.2056060	2.2964540
55	H	2.8576950	3.9467080	1.6577830
56	H	2.8942360	3.8437940	3.4274940
57	H	3.3282170	2.4314350	2.4541870
58	H	1.2100430	2.6521690	4.6834170
59	H	1.6525360	1.1566510	3.8592210
60	H	-0.0451160	1.6764320	3.9182380
61	H	0.4871770	4.6328910	3.5281430
62	H	0.3974560	4.7230430	1.7611360
63	H	-0.7806640	3.7510900	2.6670390
64	H	2.4962430	2.2783760	-3.1514800
65	H	1.7521990	3.6355820	-4.0091970
66	H	2.2618190	3.8310550	-2.3232930
67	H	-0.6066490	4.3779960	-3.4248980
68	H	-0.1245510	4.6076790	-1.7372030
69	H	-1.5030760	3.5609480	-2.1330420
70	H	-0.2162250	2.3477370	-4.6179980
71	H	0.4960790	0.9094990	-3.8886380
72	H	-1.1468130	1.4211980	-3.4353750
73	H	-2.0935730	1.4987560	1.7577330
74	H	-3.0193530	3.7407560	1.2787520
75	H	-4.4188070	4.1010880	-0.7334910
76	H	-5.0618650	-0.6001960	1.0596510
77	H	-7.4063920	-1.3498760	0.9888150
78	H	-7.9662820	-3.6254100	0.1777240
79	H	-6.1497850	-5.1468210	-0.5553980
80	H	-3.7910390	-4.3782650	-0.4946090
81	H	-4.8785140	2.2096350	-2.2703010
82	H	-3.9139270	-0.0254930	-1.8045060

Table S2. TDDFT calculation data of **Ph-PIC**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
438.20	0.0003	HOMO → LUMO	0.70445
342.27	0.5148	HOMO → LUMO+1	0.69297
311.64	0.2222	HOMO → LUMO+2	0.68658
299.71	0.1050	HOMO-1 → LUMO	0.15589
		HOMO → LUMO+3	0.66447

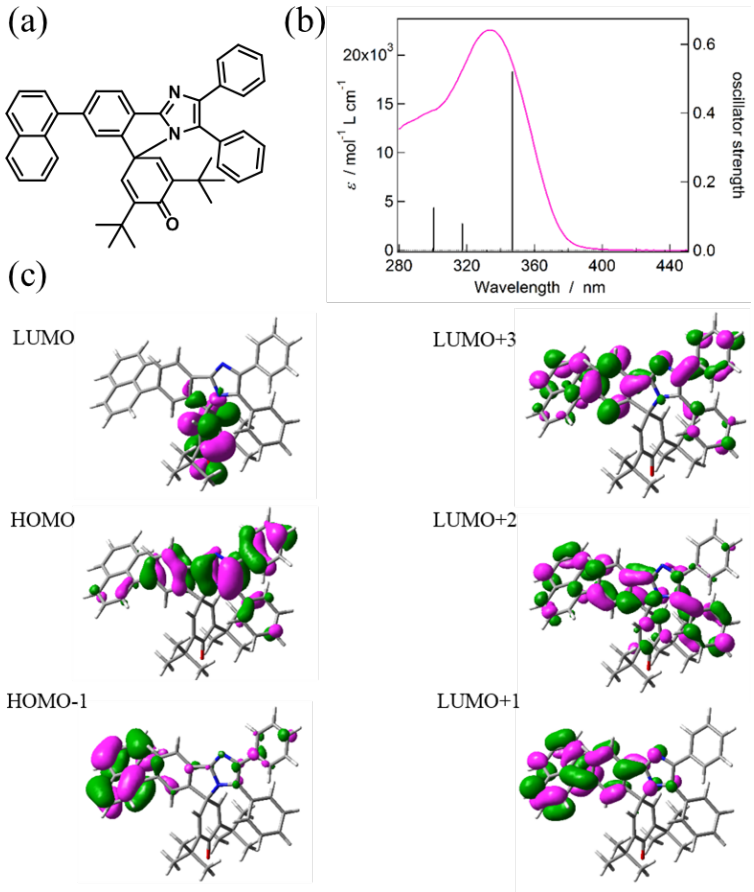

Figure S37. (a) Molecular structure of compound **Np-PIC**; (b) UV–vis absorption spectrum of **Np-PIC**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **Np-PIC**.

Table S3. Standard Orientation of the Optimized Geometry for **Np-PIC**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-3.2514890	1.2342960	0.6323260
2	C	-2.9031380	2.5693630	0.8909350
3	C	-1.5758970	2.9833490	0.9426760
4	C	-0.5826960	2.0347940	0.7324090
5	C	-0.9226250	0.7020830	0.4749370
6	C	-2.2390570	0.2871390	0.4285260
7	C	-4.6738020	0.8021820	0.6321400
8	C	0.8709930	2.1231740	0.6853570
9	C	0.3379700	-0.1614730	0.2899290
10	C	0.4169070	-0.7464070	-1.0845970
11	C	0.3566130	-2.0565610	-1.3463820
12	C	0.1722680	-3.0078550	-0.2027260
13	N	1.8046140	3.0385490	0.6974420

14	C	2.9730530	2.3512240	0.4423010
15	C	-5.6523070	1.4212700	-0.2101900
16	C	-7.0062270	0.9909810	-0.1172130
17	C	-7.3536660	-0.0506460	0.7796370
18	C	-6.3954740	-0.6531710	1.5495060
19	C	-5.0537280	-0.2202230	1.4734310
20	C	0.2651300	-2.4912560	1.2035390
21	C	0.3768010	-1.1718590	1.3944130
22	C	0.4755550	-2.6216020	-2.7597140
23	O	-0.0403170	-4.1926070	-0.4108410
24	C	0.2402040	-3.4938130	2.3554840
25	C	-1.1088970	-4.2342370	2.3799320
26	C	1.3935320	-4.5010460	2.2023680
27	C	0.4123850	-2.7904430	3.7061240
28	C	0.7688710	-1.5095330	-3.7726000
29	C	1.6448800	-3.6214200	-2.8194340
30	C	-0.8358360	-3.3113360	-3.1737300
31	C	2.7227370	0.9935250	0.2613940
32	N	1.3665070	0.8735760	0.4572250
33	C	4.2603320	3.0623790	0.3929900
34	C	3.5595610	-0.1333410	-0.1854490
35	C	3.6244090	-1.3273390	0.5384350
36	C	4.3745940	-2.3978420	0.0623930
37	C	5.0825350	-2.2800940	-1.1305440
38	C	5.4754240	2.4110360	0.6313700
39	C	6.6732760	3.1141810	0.5745250
40	C	6.6754630	4.4774060	0.2925550
41	C	5.4678730	5.1351810	0.0724610
42	C	4.2688770	4.4349510	0.1227250
43	C	5.0368300	-1.0866250	-1.8486130
44	C	4.2762680	-0.0209290	-1.3823400
45	C	-7.9879210	1.6020310	-0.9387570
46	C	-7.6467560	2.5830230	-1.8316230
47	C	-6.2979410	2.9880190	-1.9510110
48	C	-5.3274440	2.4221500	-1.1642590
49	H	-3.6944970	3.2866220	1.0698570
50	H	-1.3177380	4.0135530	1.1481850
51	H	-2.4916620	-0.7466410	0.2204150
52	H	0.5295040	-0.0119860	-1.8714250
53	H	-8.3895230	-0.3636360	0.8375080
54	H	-6.6604830	-1.4520900	2.2299510
55	H	-4.3070990	-0.6784420	2.1109920
56	H	0.4484560	-0.7399860	2.3848880
57	H	-1.1308350	-4.9133710	3.2363000
58	H	-1.9307980	-3.5219540	2.4910490
59	H	-1.2605340	-4.8105290	1.4710040
60	H	1.3780300	-5.1960180	3.0457760
61	H	2.3564080	-3.9824820	2.2106780

62	H	1.3056520	-5.0705000	1.2803510
63	H	-0.4006710	-2.0883880	3.9055190
64	H	0.4039980	-3.5422440	4.4978010
65	H	1.3629250	-2.2538420	3.7670090
66	H	0.8797440	-1.9568730	-4.7622710
67	H	-0.0453780	-0.7830030	-3.8277070
68	H	1.6979740	-0.9857200	-3.5329820
69	H	1.7583050	-3.9760820	-3.8472390
70	H	1.4681460	-4.4797050	-2.1754410
71	H	2.5763470	-3.1351790	-2.5190080
72	H	-1.6663190	-2.6013840	-3.1453650
73	H	-0.7392010	-3.6795530	-4.1984940
74	H	-1.0646400	-4.1502550	-2.5210790
75	H	3.0909180	-1.4121220	1.4762310
76	H	4.4126000	-3.3208470	0.6273480
77	H	5.6686300	-3.1129590	-1.4979120
78	H	5.4820370	1.3568130	0.8754570
79	H	7.6057910	2.5970700	0.7629860
80	H	7.6093310	5.0237810	0.2518040
81	H	5.4596930	6.1971340	-0.1397040
82	H	3.3245940	4.9366320	-0.0404600
83	H	5.5878550	-0.9885230	-2.7752960
84	H	4.2302030	0.9085280	-1.9362000
85	H	-9.0154440	1.2692880	-0.8495450
86	H	-8.4037880	3.0408420	-2.4554200
87	H	-6.0283310	3.7458600	-2.6756550
88	H	-4.2961500	2.7260560	-1.2796540

Table S4. TDDFT calculation data of **Np-PIC**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
436.97	0.0004	HOMO → LUMO	0.70362
346.96	0.5196	HOMO → LUMO+1	0.67996
317.35	0.0778	HOMO → LUMO+2	0.64062
300.60	0.1252	HOMO-1 → LUMO+3	0.66027
297.10	0.2618	HOMO-1 → LUMO+1	-0.40960
		HOMO → LUMO+3	0.50938

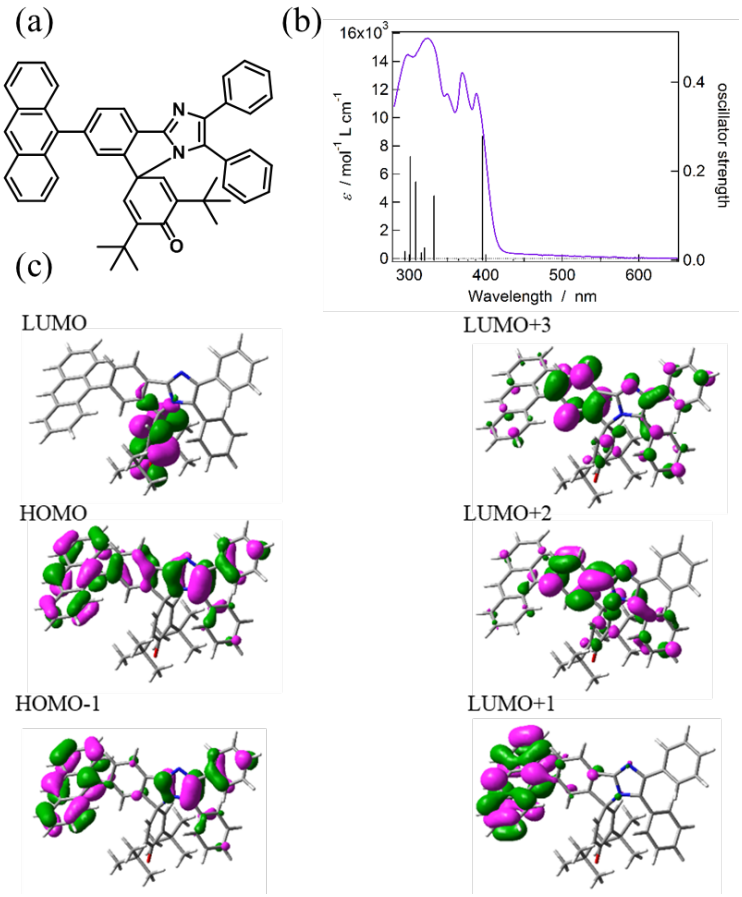

Figure S38. (a) Molecular structure of compound **An-PIC**; (b) UV–vis absorption spectrum of **An-PIC**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **An-PIC**.

Table S5. Standard Orientation of the Optimized Geometry for **An-PIC**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-2.7333330	-1.5698130	-0.3683430
2	C	-2.2997100	-2.8340480	-0.7937070
3	C	-0.9482950	-3.1302250	-0.9537240
4	C	-0.0214620	-2.1287490	-0.6934850
5	C	-0.4495420	-0.8652940	-0.2699850
6	C	-1.7872930	-0.5721840	-0.0998690
7	C	-4.1849510	-1.2713500	-0.2216010
8	C	1.4343440	-2.0860460	-0.7557020
9	C	0.7409110	0.0965560	-0.1115440
10	C	0.8850920	0.5959300	1.2900570
11	C	0.6931200	1.8689000	1.6536720
12	C	0.2969390	2.8638440	0.6039420
13	N	2.4402910	-2.9046950	-0.9214460
14	C	3.5616820	-2.1353260	-0.6887720
15	C	-4.7836040	-0.3011120	-1.0507160

16	C	-6.1776360	-0.0007040	-0.8933080
17	C	-6.9267800	-0.6875050	0.0597810
18	C	-6.3476900	-1.6533430	0.8797640
19	C	-4.9492330	-1.9461770	0.7510030
20	C	0.2995080	2.4497300	-0.8386310
21	C	0.5652560	1.1730460	-1.1372030
22	C	0.8683480	2.3499980	3.0918160
23	O	-0.0131480	4.0031770	0.9168520
24	C	0.0015270	3.5002790	-1.9054290
25	C	-1.4278510	4.0416120	-1.7171220
26	C	1.0217220	4.6489560	-1.8175450
27	C	0.0902210	2.9017530	-3.3132860
28	C	1.3675640	1.2157570	3.9935660
29	C	1.9185730	3.4746860	3.1392580
30	C	-0.4735290	2.8513200	3.6539330
31	C	3.2093520	-0.8274380	-0.3661220
32	N	1.8366410	-0.8202790	-0.4470860
33	C	4.9041840	-2.7289650	-0.7890810
34	C	3.9714230	0.3422110	0.1039280
35	C	4.7984850	0.2222630	1.2262440
36	C	5.4835920	1.3286670	1.7145950
37	C	5.3435680	2.5686270	1.0943040
38	C	6.0409060	-1.9566720	-1.0505650
39	C	7.2939300	-2.5541260	-1.1269940
40	C	7.4292410	-3.9288580	-0.9561740
41	C	6.2988200	-4.7054900	-0.7149490
42	C	5.0456410	-4.1116780	-0.6326290
43	C	4.5231550	2.6948080	-0.0232890
44	C	3.8473160	1.5859160	-0.5219500
45	C	-6.7780980	0.9959920	-1.7235610
46	C	-6.0502850	1.6545470	-2.6668800
47	C	-4.6724950	1.3407350	-2.8477420
48	C	-4.0630220	0.3963360	-2.0750900
49	C	-7.1209780	-2.3485650	1.8605560
50	C	-6.5454230	-3.2680240	2.6830790
51	C	-5.1508100	-3.5398420	2.5807450
52	C	-4.3807820	-2.9026630	1.6532670
53	H	-3.0446590	-3.5910440	-1.0063140
54	H	-0.6241670	-4.1078040	-1.2842440
55	H	-2.1072120	0.4120050	0.2242110
56	H	1.1563430	-0.1680800	2.0070530
57	H	-7.9822830	-0.4625040	0.1685090
58	H	0.5881910	0.8147240	-2.1588820
59	H	-1.6502510	4.7526700	-2.5174090
60	H	-2.1563720	3.2276310	-1.7728280
61	H	-1.5361960	4.5469450	-0.7609120
62	H	0.8153050	5.3768480	-2.6062580
63	H	2.0366700	4.2691170	-1.9663070

64	H	0.9700260	5.1534290	-0.8558600
65	H	-0.6442360	2.1057020	-3.4618050
66	H	-0.1182390	3.6866730	-4.0428150
67	H	1.0862920	2.5049290	-3.5268700
68	H	1.5043910	1.6056720	5.0040490
69	H	0.6499480	0.3936000	4.0505740
70	H	2.3290150	0.8256240	3.6493660
71	H	2.0759320	3.7713480	4.1796710
72	H	1.5938850	4.3467950	2.5765890
73	H	2.8710210	3.1229300	2.7349710
74	H	-1.2173730	2.0506810	3.6375490
75	H	-0.3334320	3.1631230	4.6923110
76	H	-0.8498810	3.6967050	3.0832400
77	H	4.8958190	-0.7431220	1.7071040
78	H	6.1214690	1.2249520	2.5832140
79	H	5.8716060	3.4314980	1.4799120
80	H	5.9427900	-0.8905000	-1.2076970
81	H	8.1649710	-1.9440540	-1.3316910
82	H	8.4060240	-4.3918230	-1.0187480
83	H	6.3935950	-5.7769930	-0.5889790
84	H	4.1595790	-4.7049010	-0.4503370
85	H	4.4139560	3.6550190	-0.5117830
86	H	3.2221040	1.6808160	-1.4005270
87	H	-7.8302650	1.2129130	-1.5817200
88	H	-6.5137220	2.4093780	-3.2889660
89	H	-4.1064340	1.8534240	-3.6156140
90	H	-3.0213050	0.1578260	-2.2400360
91	H	-8.1776580	-2.1200160	1.9351410
92	H	-7.1390190	-3.7882640	3.4237600
93	H	-4.6984950	-4.2563840	3.2545850
94	H	-3.3207910	-3.1077080	1.5986390

Table S6. TDDFT calculation data of **An-PIC**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
435.87	0.0006	HOMO-1 → LUMO	0.23646
		HOMO → LUMO	0.66157
395.81	0.2781	HOMO → LUMO+1	0.67967
332.41	0.1443	HOMO → LUMO+2	0.68728
308.63	0.1759	HOMO-1 → LUMO+2	-0.39268
		HOMO → LUMO+3	0.42256

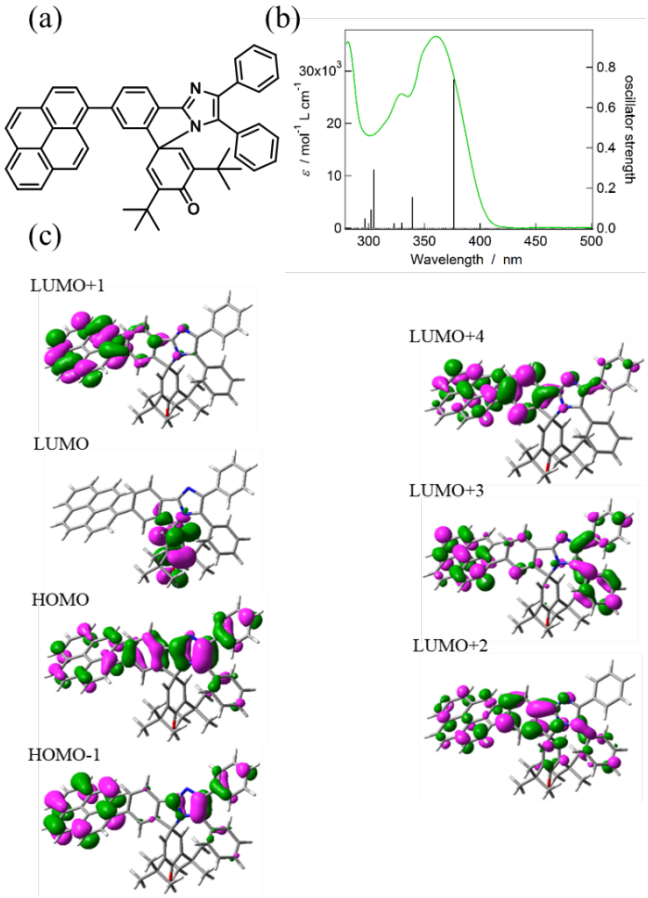

Figure S39. (a) Molecular structure of compound **Py-PIC**; (b) UV–vis absorption spectrum of **Py-PIC**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **Py-PIC**.

Table S7. Standard Orientation of the Optimized Geometry for **Py-PIC**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.3003110	0.8577890	-0.8957830
2	C	2.0450290	2.1969310	-1.2310020
3	C	0.7526570	2.7121930	-1.2559150
4	C	-0.3003370	1.8615110	-0.9435120
5	C	-0.0536600	0.5251970	-0.6091370
6	C	1.2271860	0.0098730	-0.5880210
7	C	3.6805830	0.3088370	-0.9299550
8	C	-1.7400290	2.0668400	-0.8524580
9	C	-1.3679600	-0.2212370	-0.3176050
10	C	-1.4394280	-0.6879640	1.1018990
11	C	-1.4625490	-1.9740640	1.4680350
12	C	-1.3871890	-3.0233400	0.4005660

13	N	-2.6001130	3.0510750	-0.8866620
14	C	-3.8069600	2.4744530	-0.5482650
15	C	4.7467640	0.8881100	-0.2109710
16	C	6.0502700	0.3316050	-0.3389630
17	C	6.2693150	-0.8032700	-1.1623650
18	C	5.1842190	-1.3723690	-1.8329310
19	C	3.9176590	-0.8227190	-1.7154670
20	C	-1.4987950	-2.6138780	-1.0390900
21	C	-1.5225350	-1.3091760	-1.3340710
22	C	-1.5705110	-2.4154270	2.9253460
23	O	-1.2453660	-4.1998830	0.6967810
24	C	-1.5782200	-3.7022800	-2.1071670
25	C	-0.2736830	-4.5194100	-2.1182620
26	C	-2.7787590	-4.6257890	-1.8345520
27	C	-1.7635390	-3.0973340	-3.5030510
28	C	-1.7485610	-1.2085190	3.8530920
29	C	-2.8037490	-3.3199800	3.0999550
30	C	-0.2966920	-3.1637770	3.3547830
31	C	-3.6546190	1.1140490	-0.2951040
32	N	-2.3207980	0.8756870	-0.5318040
33	C	-5.0304580	3.2890110	-0.4870270
34	C	-4.5566320	0.0793110	0.2402270
35	C	-5.2019840	0.2963950	1.4629790
36	C	-6.0204030	-0.6852330	2.0092560
37	C	-6.1968410	-1.8978160	1.3457640
38	C	-6.3040510	2.7287860	-0.6334480
39	C	-7.4373450	3.5305420	-0.5588350
40	C	-7.3164560	4.9014570	-0.3498110
41	C	-6.0506130	5.4677150	-0.2225900
42	C	-4.9158080	4.6692910	-0.2912840
43	C	-5.5604280	-2.1191840	0.1275250
44	C	-4.7514270	-1.1327760	-0.4276840
45	C	7.1500900	0.9092430	0.3645470
46	C	6.9465610	2.0287420	1.2104470
47	C	5.6136940	2.5438700	1.3558780
48	C	4.5689490	2.0020040	0.6860930
49	C	7.5984440	-1.3382040	-1.2844430
50	C	8.6409760	-0.7803320	-0.6267680
51	C	8.4536520	0.3634890	0.2242970
52	C	9.5175440	0.9482550	0.9174820
53	C	9.3095480	2.0489490	1.7405960
54	C	8.0357650	2.5841510	1.8889050
55	H	2.8803030	2.8339860	-1.4940470
56	H	0.5656100	3.7439640	-1.5216970
57	H	1.4070640	-1.0259860	-0.3221790
58	H	-1.4725710	0.1138160	1.8281650
59	H	5.3444700	-2.2412600	-2.4601420
60	H	3.0901480	-1.2548690	-2.2651730

61	H	-1.5988310	-0.9521090	-2.3534850
62	H	-0.3220260	-5.2643450	-2.9169090
63	H	0.5809420	-3.8663720	-2.3147310
64	H	-0.1186150	-5.0297620	-1.1713240
65	H	-2.8426460	-5.3768600	-2.6259600
66	H	-3.7095680	-4.0517800	-1.8386740
67	H	-2.6818030	-5.1346030	-0.8786670
68	H	-0.9190830	-2.4655710	-3.7884170
69	H	-1.8325050	-3.9077090	-4.2312140
70	H	-2.6820000	-2.5081700	-3.5718930
71	H	-1.8528030	-1.5667800	4.8791170
72	H	-0.8854500	-0.5388930	3.8234050
73	H	-2.6479830	-0.6404030	3.6015640
74	H	-2.9078520	-3.5813290	4.1563150
75	H	-2.7079350	-4.2381490	2.5248240
76	H	-3.7088940	-2.7943630	2.7852380
77	H	0.5795920	-2.5198540	3.2453450
78	H	-0.3829450	-3.4431150	4.4081950
79	H	-0.1501590	-4.0654000	2.7651010
80	H	-5.0549600	1.2399280	1.9737110
81	H	-6.5153060	-0.5063900	2.9552930
82	H	-6.8285100	-2.6650080	1.7752540
83	H	-6.4074410	1.6678110	-0.8192490
84	H	-8.4166140	3.0832530	-0.6756580
85	H	-8.2006980	5.5239690	-0.2947790
86	H	-5.9466060	6.5345520	-0.0680210
87	H	-3.9271120	5.0983600	-0.1988050
88	H	-5.7009770	-3.0568060	-0.3954240
89	H	-4.2728450	-1.2974280	-1.3844760
90	H	5.4565260	3.3769300	2.0308620
91	H	3.5726510	2.3941700	0.8350220
92	H	7.7444190	-2.2029410	-1.9208960
93	H	9.6397560	-1.1884680	-0.7257590
94	H	10.5110200	0.5303150	0.8061530
95	H	10.1440110	2.4896190	2.2709890
96	H	7.8735810	3.4386450	2.5352270

Table S8. TDDFT calculation data of **Py-PIC**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
438.07	0.0004	HOMO-1 → LUMO	0.18582
		HOMO → LUMO	0.67923
376.37	0.7384	HOMO → LUMO+1	0.68946
339.45	0.1544	HOMO-1 → LUMO+1	0.62196
304.81	0.2898	HOMO → LUMO+3	0.36602
		HOMO → LUMO+4	0.49875

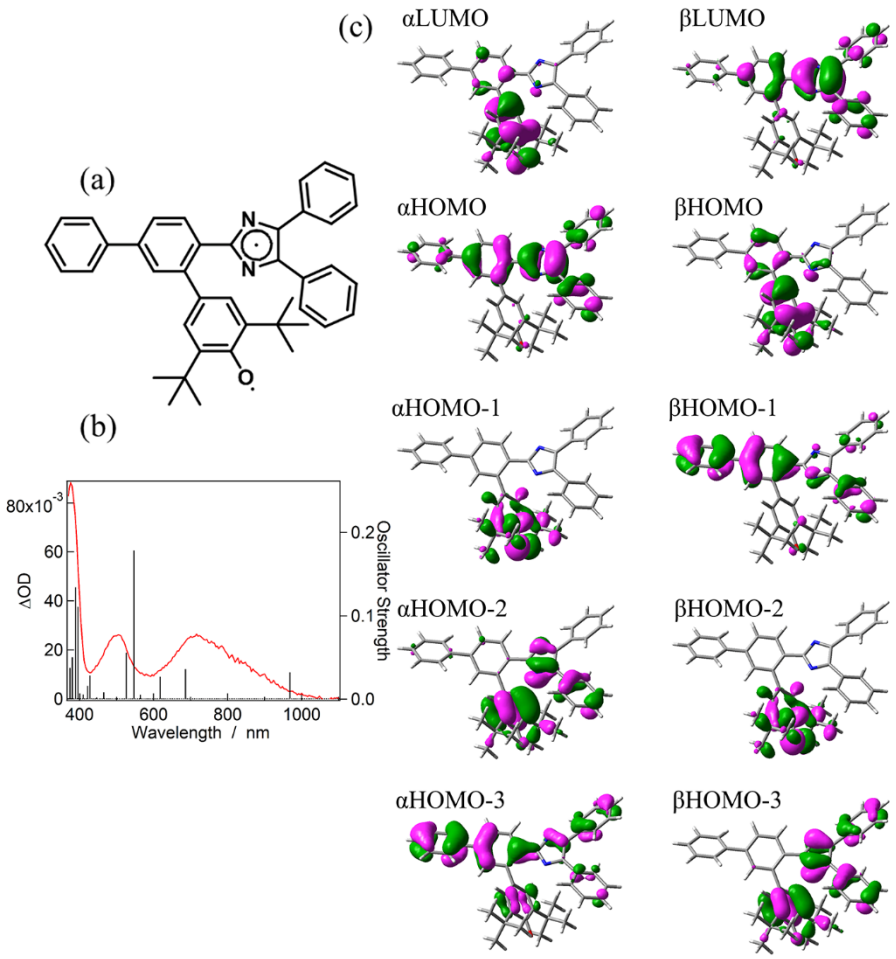

Figure S40. (a) Molecular structure of compound **Ph-PICR**; (b) UV–vis absorption spectrum of **Ph-PICR**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **Ph-PICR**.

Table S9. Standard Orientation of the Optimized Geometry for **Ph-PICR**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.9225260	-1.8181870	-0.0025820
2	C	1.8011300	-0.7063530	-0.0619600
3	C	-0.5079350	-1.6849270	0.1668340
4	N	-1.3600630	-2.7376520	-0.0211260
5	C	-2.5562760	-2.2399990	0.2364210
6	C	-2.3974840	-0.8066240	0.5711960
7	N	-1.1067900	-0.5279240	0.5568580
8	C	-3.7495260	-3.0849260	0.2346560
9	C	-3.3779820	0.2521040	0.8021710

10	C	-4.8224060	-2.8439700	1.1025650
11	C	-5.9164470	-3.7006560	1.1157900
12	C	-5.9535780	-4.8007960	0.2632710
13	C	-4.8840810	-5.0529160	-0.5947490
14	C	-3.7843540	-4.2072000	-0.6042120
15	C	-4.6615260	0.2160760	0.2411710
16	C	-5.5285060	1.2891220	0.4124520
17	C	-5.1267460	2.4050530	1.1414070
18	C	-3.8455670	2.4540670	1.6902120
19	C	-2.9724610	1.3911920	1.5149990
20	C	1.3434400	0.6841630	-0.2316840
21	C	0.4203190	1.0156730	-1.2527350
22	C	-0.0187100	2.2948440	-1.4496500
23	C	0.5030670	3.3565360	-0.5722070
24	C	1.4791730	3.0070940	0.4772540
25	C	1.8733420	1.6959250	0.5930340
26	O	0.1287100	4.5364550	-0.7126400
27	C	-1.0386400	2.6476080	-2.5273630
28	C	1.9983770	4.0975170	1.4066260
29	C	0.8230730	4.7271210	2.1785890
30	C	2.7308170	5.1821630	0.5943230
31	C	2.9867710	3.5406200	2.4379810
32	C	-2.3053420	3.2374800	-1.8781170
33	C	-1.4660040	1.4077980	-3.3212220
34	C	-0.4361910	3.6600340	-3.5185630
35	C	3.1783530	-0.9422510	-0.0335480
36	C	3.7125290	-2.2314160	-0.0071820
37	C	2.8281560	-3.3214000	-0.0115290
38	C	1.4628160	-3.1161420	-0.0084340
39	H	-4.7867960	-2.0003430	1.7792040
40	H	-6.7365590	-3.5122920	1.7965770
41	H	-6.8093690	-5.4637810	0.2719670
42	H	-4.9085420	-5.9114280	-1.2536250
43	H	-2.9398840	-4.3948520	-1.2535730
44	H	-4.9682740	-0.6369100	-0.3491980
45	H	-6.5140500	1.2574840	-0.0339720
46	H	-5.8043250	3.2391860	1.2717320
47	H	-3.5246570	3.3276850	2.2429120
48	H	-1.9646420	1.4246700	1.9070310
49	H	0.0639260	0.2096330	-1.8771480
50	H	2.5702580	1.3971410	1.3633280
51	H	0.2978730	3.9647740	2.7602800
52	H	1.2088290	5.4785520	2.8727790
53	H	0.1206180	5.2020840	1.4983740
54	H	3.5734860	4.7475450	0.0507240
55	H	2.0592880	5.6587620	-0.1147710
56	H	3.1224410	5.9401400	1.2782000
57	H	3.8677100	3.1031660	1.9618340

58	H	3.3260510	4.3592820	3.0758670
59	H	2.5228450	2.7877660	3.0795670
60	H	-2.0760160	4.1430650	-1.3216570
61	H	-3.0275260	3.4796740	-2.6631160
62	H	-2.7646530	2.5109520	-1.2036020
63	H	-0.6240910	0.9482270	-3.8447890
64	H	-1.9323030	0.6590030	-2.6753810
65	H	-2.2014020	1.7075520	-4.0709320
66	H	0.4576600	3.2454830	-3.9915680
67	H	-1.1672340	3.8749820	-4.3027950
68	H	-0.1737320	4.5883730	-3.0173210
69	H	3.8478850	-0.0947270	-0.1145070
70	H	3.2213040	-4.3291850	0.0254830
71	H	0.7749290	-3.9493570	0.0322850
72	C	5.1783670	-2.4399520	-0.0009050
73	C	5.7523240	-3.4916990	-0.7229850
74	C	6.0164100	-1.5872080	0.7255030
75	C	7.1287610	-3.6852450	-0.7188590
76	C	7.3926850	-1.7812650	0.7297490
77	H	5.5823180	-0.7857660	1.3107040
78	C	7.9534260	-2.8306670	0.0071740
79	H	8.0264000	-1.1175430	1.3042010
80	H	9.0252840	-2.9816830	0.0102980
81	H	5.1185400	-4.1419910	-1.3131850
82	H	7.5581000	-4.4982500	-1.2905520

Table S10. TDDFT calculation data of **Ph-PICR**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
968.46	0.0323	αHOMO → αLUMO	-0.14839
		βHOMO → βLUMO	0.97786
686.18	0.0361	αHOMO → αLUMO	0.96243
618.11	0.0269	βHOMO-4 → βLUMO	-0.30956
		βHOMO-3 → βLUMO	0.82345
547.07	0.1786	βHOMO-8 → βLUMO	0.27396
		βHOMO-4 → βLUMO	-0.29532
		βHOMO-1 → βLUMO	0.81201
526.20	0.0557	βHOMO-10 → βLUMO	-0.47794
		βHOMO-4 → βLUMO	0.59161
		βHOMO-1 → βLUMO	0.39232

SCF Done: E(UM052X) = -1769.79689772 A.U.
S**2 before annihilation 1.0369, after 0.6379

Zero-point correction = 0.693485 (Hartree/Particle)

Thermal correction to Energy	=	0.731834
Thermal correction to Enthalpy	=	0.732779
Thermal correction to Gibbs Free Energy	=	0.618867
Sum of electronic and zero-point Energies	=	-1769.103412
Sum of electronic and thermal Energies	=	-1769.065063
Sum of electronic and thermal Enthalpies	=	-1769.064119
Sum of electronic and thermal Free Energies	=	-1769.178031

Low frequencies ---	-7.4100	-3.3652	-0.0005	0.0006	0.0009	3.0031
Low frequencies ---	5.1387	12.0223	19.6317			

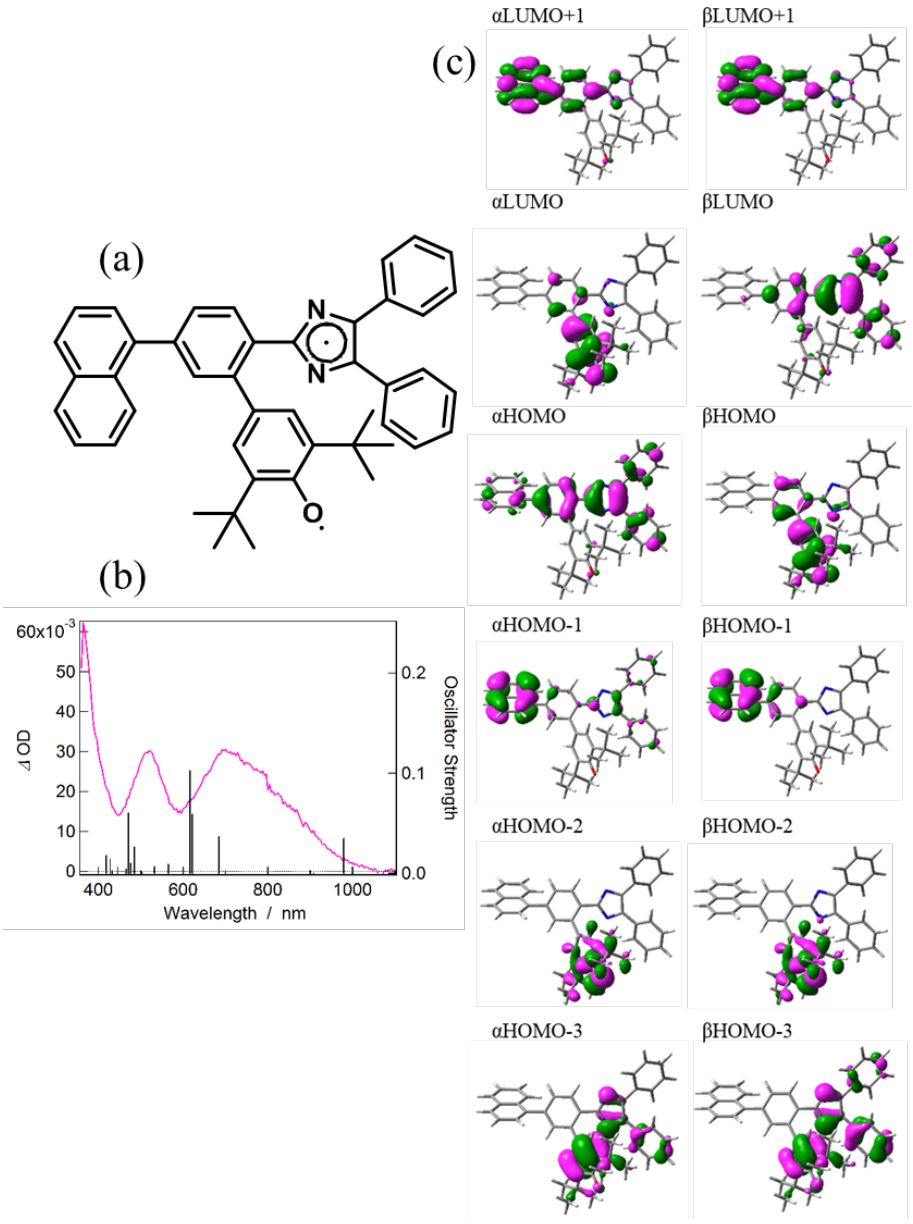

Figure S41. (a) Molecular structure of compound **Np-PICR**; (b) UV–vis absorption spectrum of **Np-PICR**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **Np-PICR**.

Table S11. Standard Orientation of the Optimized Geometry for **Np-PICR**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-0.7822650	1.2846910	0.3241390
2	C	-1.3094390	-0.0315280	0.3420820
3	C	0.6089080	1.5747220	0.0489670
4	N	1.1647690	2.7901200	0.3344520
5	C	2.4234960	2.6719320	-0.0502110
6	C	2.6187950	1.3017750	-0.5753730
7	N	1.4544160	0.6809980	-0.5333460
8	C	3.3521360	3.7987270	0.0175980
9	C	3.8213380	0.5892850	-1.0040020
10	C	4.3843460	3.9592360	-0.9161060
11	C	5.2222840	5.0655800	-0.8483280
12	C	5.0419210	6.0194510	0.1497100
13	C	4.0074480	5.8737970	1.0729170
14	C	3.1611070	4.7766660	1.0035640
15	C	3.6750670	-0.5026020	-1.8727860
16	C	4.7801270	-1.2540800	-2.2430830
17	C	6.0410480	-0.9406800	-1.7364710
18	C	6.1906100	0.1257650	-0.8541940
19	C	5.0888530	0.8900590	-0.4876870
20	C	-0.4752700	-1.2440720	0.3533190
21	C	-0.8147170	-2.3347650	-0.4730300
22	C	-0.0741430	-3.4914240	-0.4900450
23	C	1.0904210	-3.5945680	0.4099410
24	C	1.4199520	-2.4587520	1.2879900
25	C	0.6284920	-1.3466260	1.2357120
26	O	1.7806080	-4.6308900	0.4263300
27	C	-0.4067090	-4.6534920	-1.4181210
28	C	2.6350360	-2.5476640	2.2051220
29	C	3.9097980	-2.7506740	1.3634760
30	C	2.4706200	-3.7114350	3.1989460
31	C	2.8222060	-1.2585840	3.0136170
32	C	0.7747660	-4.9180030	-2.3704910
33	C	-1.6407660	-4.3555740	-2.2776130
34	C	-0.7068320	-5.9202920	-0.5943550
35	C	-2.6980340	-0.1896690	0.4239550
36	C	-3.5638460	0.8950640	0.5445060
37	C	-3.0182940	2.1883350	0.5987090
38	C	-1.6547900	2.3753400	0.4905290
39	H	4.5152280	3.2289660	-1.7036110
40	H	6.0118360	5.1854840	-1.5788990
41	H	5.6998940	6.8774150	0.2041010
42	H	3.8610810	6.6183050	1.8449350
43	H	2.3468020	4.6531960	1.7046490
44	H	2.6847000	-0.7496150	-2.2310770

45	H	4.6591410	-2.0923790	-2.9169510
46	H	6.9013300	-1.5335930	-2.0198420
47	H	7.1641130	0.3571500	-0.4415060
48	H	5.2051660	1.7012720	0.2184660
49	H	-1.6583210	-2.2159460	-1.1383820
50	H	0.8317530	-0.4992430	1.8738200
51	H	4.0476740	-1.9172640	0.6706590
52	H	4.7755210	-2.7871170	2.0308650
53	H	3.8633560	-3.6783220	0.7983690
54	H	1.5776770	-3.5671750	3.8126380
55	H	2.3923670	-4.6622790	2.6776380
56	H	3.3384340	-3.7429340	3.8634210
57	H	1.9710150	-1.0597780	3.6695350
58	H	3.7088290	-1.3645120	3.6423420
59	H	2.9758810	-0.3944870	2.3612240
60	H	1.6672010	-5.1982950	-1.8167170
61	H	0.5105770	-5.7300740	-3.0532610
62	H	0.9892670	-4.0276740	-2.9672500
63	H	-2.5301180	-4.1858780	-1.6656890
64	H	-1.4873040	-3.4877060	-2.9233720
65	H	-1.8379940	-5.2170390	-2.9189090
66	H	-1.5520020	-5.7479420	0.0767500
67	H	-0.9734430	-6.7341450	-1.2740810
68	H	0.1575040	-6.2190020	-0.0074000
69	H	-3.1108630	-1.1911860	0.4317160
70	H	-3.6760630	3.0383440	0.7293770
71	H	-1.2264250	3.3680160	0.5056420
72	C	-5.0236280	0.6677460	0.6932910
73	C	-5.9759650	1.3222290	-0.1525880
74	C	-5.4661200	-0.1856510	1.6801390
75	C	-5.5991020	2.1508120	-1.2431810
76	C	-7.3630400	1.1041750	0.0820370
77	C	-6.8431650	-0.4087960	1.8978170
78	H	-4.7388320	-0.6679730	2.3218320
79	C	-6.5463300	2.7581760	-2.0272820
80	H	-4.5495820	2.2879210	-1.4644800
81	C	-8.3179880	1.7523940	-0.7423880
82	C	-7.7718170	0.2323940	1.1228890
83	H	-7.1562540	-1.0768710	2.6896800
84	C	-7.9228680	2.5673660	-1.7697840
85	H	-6.2378570	3.3824820	-2.8561260
86	H	-9.3700640	1.5827370	-0.5453490
87	H	-8.8319400	0.0801050	1.2876380
88	H	-8.6603110	3.0556120	-2.3939020

Table S12. TDDFT calculation data of **Np-PICR**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
979.51	0.0348	βHOMO → βLUMO	0.97555
684.33	0.0367	αHOMO → αLUMO	0.94515
622.17	0.0591	βHOMO-3 → βLUMO βHOMO-1 → βLUMO	0.65467 0.60938
615.97	0.1026	βHOMO-3 → βLUMO βHOMO → βLUMO	-0.49811 0.73158
484.65	0.0265	αHOMO-1 → αLUMO+1 βHOMO-1 → βLUMO+1	-0.48404 0.53616
475.56	0.0101	αHOMO-1 → αLUMO βHOMO-6 → βLUMO	0.69675 0.52008
470.70	0.0604	αHOMO-1 → αLUMO βHOMO-1 → βLUMO	0.64910 -0.63695
418.81	0.0180	βHOMO-5 → βLUMO	0.76779

SCF Done: E(UM052X) = -1923.42844063 A.U.
S**2 before annihilation 1.0277, after 0.6234

Zero-point correction	=	0.740818 (Hartree/Particle)
Thermal correction to Energy	=	0.781838
Thermal correction to Enthalpy	=	0.782782
Thermal correction to Gibbs Free Energy	=	0.662524
Sum of electronic and zero-point Energies	=	-1922.687623
Sum of electronic and thermal Energies	=	-1922.646603
Sum of electronic and thermal Enthalpies	=	-1922.645659
Sum of electronic and thermal Free Energies	=	-1922.765916

Low frequencies --- -6.2779 -3.0795 -0.0007 -0.0006 0.0011 2.0687
Low frequencies --- 5.8237 10.5221 19.5606

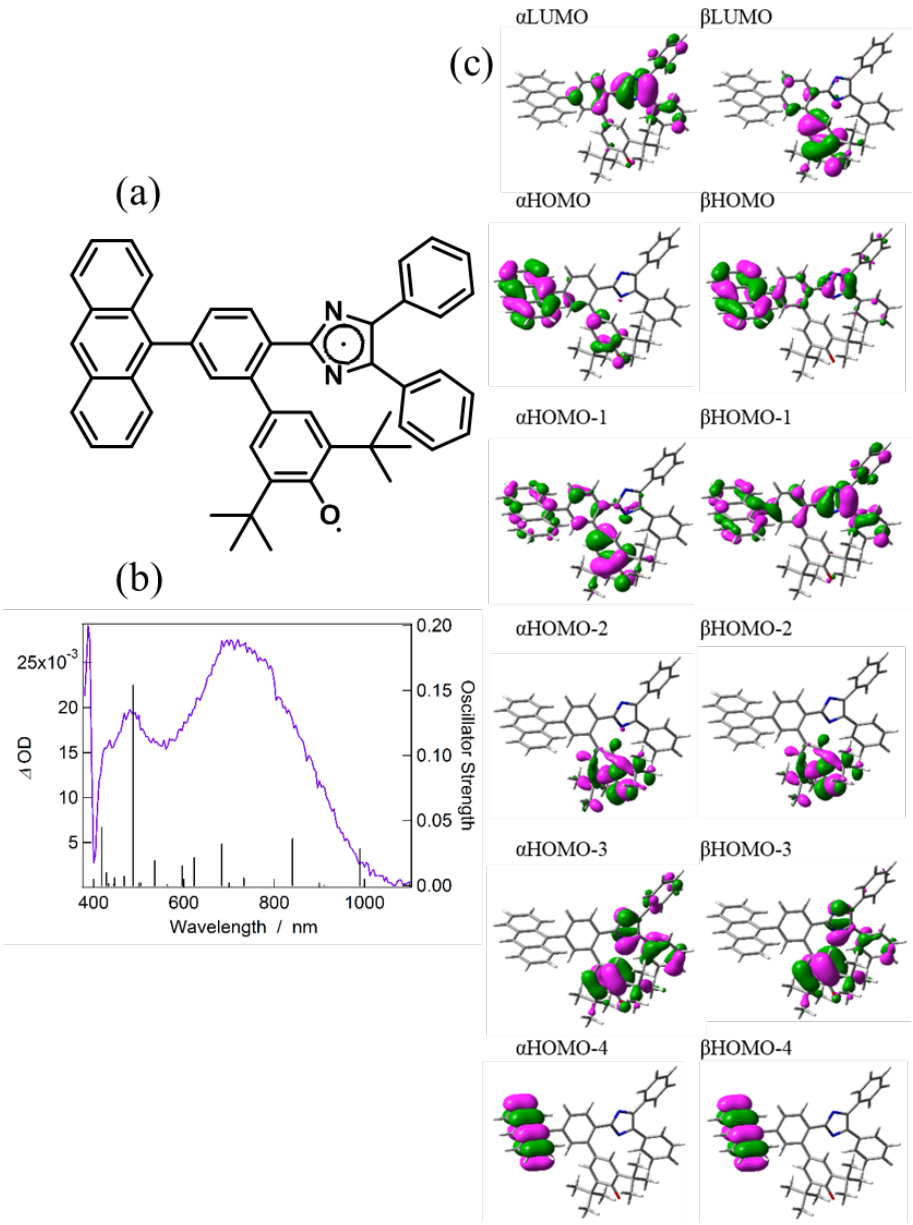

Figure S42. (a) Molecular structure of compound **An-PICR**; (b) UV–vis absorption spectrum of **An-PICR**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **An-PICR**.

Table S13. Standard Orientation of the Optimized Geometry for **An-PICR**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.2936300	-1.4040930	0.1653170
2	C	0.8961750	-0.1227650	0.0906750
3	C	-1.1313120	-1.6097030	0.0067610
4	N	-1.7394260	-2.7844370	0.3492750
5	C	-3.0124760	-2.5918700	0.0505170
6	C	-3.1601060	-1.2157980	-0.4761000
7	N	-1.9586820	-0.6702440	-0.5243040
8	C	-3.9992570	-3.6613200	0.1879030
9	C	-4.3398580	-0.4272450	-0.8252020
10	C	-5.0911640	-3.7685000	-0.6833610
11	C	-5.9820490	-4.8277360	-0.5600780
12	C	-5.7955880	-5.7863430	0.4322800
13	C	-4.7040130	-5.6928470	1.2944700
14	C	-3.8050140	-4.6435820	1.1688560
15	C	-4.1755230	0.6675750	-1.6879000
16	C	-5.2492380	1.4941800	-1.9814560
17	C	-6.4961090	1.2523340	-1.4053010
18	C	-6.6621090	0.1825860	-0.5300250
19	C	-5.5920690	-0.6556280	-0.2386500
20	C	0.1323870	1.1364780	0.1189440
21	C	0.4290500	2.1554340	-0.8071970
22	C	-0.2609580	3.3437960	-0.8232100
23	C	-1.3132010	3.5601390	0.1871370
24	C	-1.5882620	2.5019080	1.1739070
25	C	-0.8595150	1.3481750	1.1084660
26	O	-1.9568370	4.6265030	0.2044860
27	C	0.0141990	4.4277910	-1.8579000
28	C	-2.6822820	2.7145280	2.2147010
29	C	-4.0386270	2.9247920	1.5139180
30	C	-2.3497350	3.9347200	3.0926690
31	C	-2.8251570	1.4963390	3.1341790
32	C	-1.2547990	4.6870830	-2.6923710
33	C	1.1311730	4.0177240	-2.8243960
34	C	0.4540420	5.7276230	-1.1580600
35	C	2.2929380	-0.0455190	0.0561490
36	C	3.0979490	-1.1785220	0.1560730
37	C	2.4869340	-2.4328410	0.2977720
38	C	1.1088580	-2.5409650	0.3002920
39	H	-5.2270260	-3.0355230	-1.4676570
40	H	-6.8176090	-4.9077630	-1.2433750
41	H	-6.4939540	-6.6077930	0.5294230
42	H	-4.5538220	-6.4411790	2.0620390
43	H	-2.9456010	-4.5623460	1.8206050
44	H	-3.1938070	0.8580350	-2.1008730

45	H	-5.1131210	2.3353510	-2.6488820
46	H	-7.3314100	1.9037230	-1.6286020
47	H	-7.6227570	0.0063780	-0.0634590
48	H	-5.7188170	-1.4678270	0.4643310
49	H	1.1914970	1.9541400	-1.5466880
50	H	-1.0308160	0.5501670	1.8163430
51	H	-4.2979370	2.0519560	0.9101950
52	H	-4.8148450	3.0587600	2.2726520
53	H	-4.0171750	3.8040380	0.8747810
54	H	-1.3987650	3.7849730	3.6103090
55	H	-2.2887700	4.8405780	2.4944630
56	H	-3.1312260	4.0606070	3.8470000
57	H	-1.9085080	1.2991920	3.6954650
58	H	-3.6216870	1.6916690	3.8552440
59	H	-3.0954200	0.5982730	2.5721510
60	H	-2.0670840	5.0462640	-2.0655840
61	H	-1.0359020	5.4380480	-3.4563080
62	H	-1.5711170	3.7706250	-3.1978030
63	H	2.0755290	3.8427720	-2.3034620
64	H	0.8704380	3.1204380	-3.3905680
65	H	1.2910920	4.8275370	-3.5391790
66	H	1.3599820	5.5569990	-0.5710870
67	H	0.6773970	6.4845180	-1.9149070
68	H	-0.3279220	6.1024430	-0.5028380
69	H	2.7639710	0.9288750	0.0008150
70	H	3.1066300	-3.3159700	0.3916180
71	H	0.6250420	-3.5051560	0.3761080
72	C	4.5820700	-1.0534510	0.1356860
73	C	5.3051960	-1.5292160	-0.9747020
74	C	5.2516250	-0.4630510	1.2245560
75	C	4.6671840	-2.1094460	-2.1179210
76	C	6.7347900	-1.4125400	-0.9890620
77	C	6.6806450	-0.3399680	1.1911110
78	C	4.5645610	0.0049060	2.3907370
79	C	5.3984110	-2.5605230	-3.1766510
80	H	3.5881360	-2.1793730	-2.1363400
81	C	7.4639590	-1.9002540	-2.1173620
82	C	7.3870640	-0.8195280	0.0901120
83	C	7.3551540	0.2671720	2.2954960
84	H	3.4904260	-0.1071190	2.4455080
85	C	5.2449180	0.5747090	3.4255920
86	C	6.8197290	-2.4612570	-3.1775870
87	H	4.8959450	-2.9942390	-4.0318090
88	H	8.5437350	-1.8084680	-2.1076490
89	H	8.4678680	-0.7283640	0.0723190
90	C	6.6619150	0.7160710	3.3779230
91	H	8.4340650	0.3582710	2.2490860
92	H	4.7057820	0.9204680	4.2983720

93	H	7.3805940	-2.8270140	-4.0281370
94	H	7.1815990	1.1744750	4.2094710

Table S14. TDDFT calculation data of **An-PICR**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
979.51	0.0348	βHOMO → βLUMO	0.97555
684.33	0.0367	αHOMO → αLUMO	0.94515
622.17	0.0591	βHOMO-3 → βLUMO βHOMO-1 → βLUMO	0.65467 0.60938
615.97	0.1026	βHOMO-3 → βLUMO βHOMO → βLUMO	-0.49811 0.73158
484.65	0.0265	αHOMO-1 → αLUMO+1 βHOMO-1 → βLUMO+1	-0.48404 0.53616
475.56	0.0101	αHOMO-1 → αLUMO βHOMO-6 → βLUMO	0.69675 0.52008
470.70	0.0604	αHOMO-1 → αLUMO βHOMO-1 → βLUMO	0.64910 -0.63695
418.81	0.0180	βHOMO-5 → βLUMO	0.76779

SCF Done: E(UM052X) = -2077.05328659 A.U.
S**2 before annihilation 1.0342, after 0.6301

Zero-point correction	=	0.788160 (Hartree/Particle)
Thermal correction to Energy	=	0.831994
Thermal correction to Enthalpy	=	0.832938
Thermal correction to Gibbs Free Energy	=	0.707804
Sum of electronic and zero-point Energies	=	-2076.265127
Sum of electronic and thermal Energies	=	-2076.221293
Sum of electronic and thermal Enthalpies	=	-2076.220349
Sum of electronic and thermal Free Energies	=	-2076.345483

Low frequencies --- -6.6677 -4.5312 -0.0001 0.0005 0.0014 4.4651

Low frequencies --- 9.2518 10.5456 12.9944

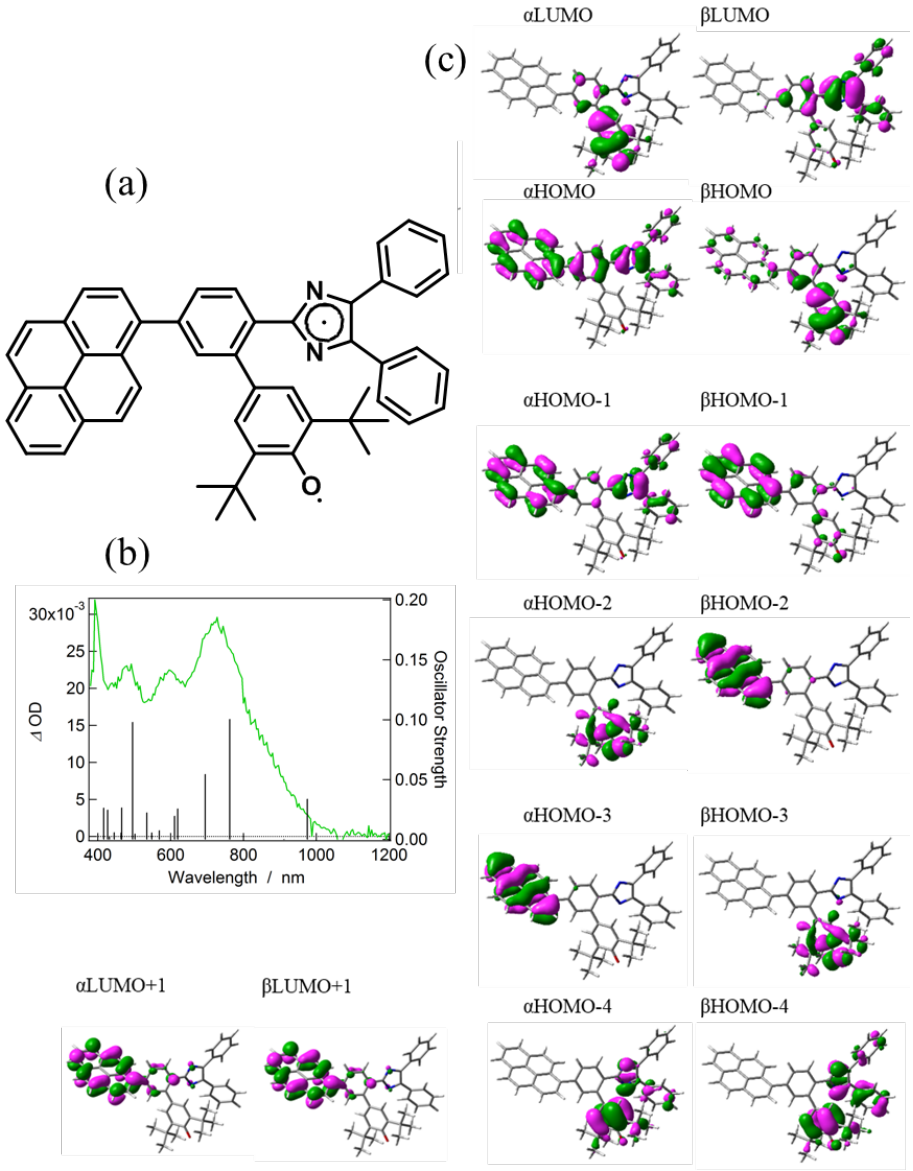

Figure S43. (a) Molecular structure of compound **Py-PICR**; (b) UV–vis absorption spectrum of **Py-PICR**. The calculated spectra are shown by the perpendicular lines. (c) The calculated molecular orbitals of **Py-PICR**.

Table S15. Standard Orientation of the Optimized Geometry for **Py-PICR**

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.1621630	1.0983850	0.4298910
2	C	-0.2369590	-0.2628020	0.4049870
3	C	1.5082430	1.5403660	0.1335070
4	N	1.9390890	2.7945750	0.4605250
5	C	3.1930750	2.8296940	0.0446630
6	C	3.5184070	1.5120560	-0.5453210
7	N	2.4296540	0.7669840	-0.5062490

8	C	3.9945740	4.0481970	0.1404630
9	C	4.7808610	0.9590510	-1.0338240
10	C	5.0017770	4.3463870	-0.7868200
11	C	5.7063350	5.5405060	-0.6925540
12	C	5.4165240	6.4458030	0.3247360
13	C	4.4073610	6.1608090	1.2436280
14	C	3.6942760	4.9748280	1.1487950
15	C	4.7405690	-0.0639450	-1.9919480
16	C	5.9142660	-0.6659570	-2.4212310
17	C	7.1396370	-0.2717210	-1.8849510
18	C	7.1853390	0.7261200	-0.9153040
19	C	6.0141480	1.3425610	-0.4907020
20	C	0.7021110	-1.3937190	0.3353300
21	C	0.4126050	-2.4887000	-0.5051450
22	C	1.2381960	-3.5830160	-0.5859790
23	C	2.4499160	-3.6127460	0.2545080
24	C	2.7342780	-2.4717150	1.1416820
25	C	1.8544750	-1.4262460	1.1590680
26	O	3.2165610	-4.5932560	0.2149400
27	C	0.9467210	-4.7508300	-1.5204750
28	C	3.9999420	-2.4804280	1.9922580
29	C	5.2390370	-2.5684300	1.0801840
30	C	3.9795860	-3.6706270	2.9682300
31	C	4.1303940	-1.1948680	2.8173050
32	C	2.0941920	-4.9116820	-2.5354610
33	C	-0.3476970	-4.5322370	-2.3122440
34	C	0.7836630	-6.0491680	-0.7073090
35	C	-1.6012250	-0.5551160	0.5265650
36	C	-2.5621360	0.4352840	0.7187160
37	C	-2.1401430	1.7717470	0.8123750
38	C	-0.8049060	2.0919790	0.6709230
39	H	5.2150220	3.6549610	-1.5909930
40	H	6.4765510	5.7668590	-1.4186680
41	H	5.9699710	7.3733790	0.3980530
42	H	4.1763720	6.8662220	2.0315760
43	H	2.8998550	4.7415710	1.8447180
44	H	3.7785300	-0.3771810	-2.3748100
45	H	5.8748760	-1.4513690	-3.1650100
46	H	8.0537270	-0.7489990	-2.2143400
47	H	8.1325810	1.0191340	-0.4812110
48	H	6.0511650	2.1018470	0.2794730
49	H	-0.4688560	-2.4232740	-1.1273770
50	H	2.0220960	-0.5819600	1.8109850
51	H	5.2691890	-1.7195060	0.3928460
52	H	6.1403460	-2.5387020	1.6989450
53	H	5.2380520	-3.4914860	0.5057410
54	H	3.1160230	-3.6037580	3.6349650
55	H	3.9403810	-4.6151520	2.4312400

56	H	4.8846620	-3.6498150	3.5814560
57	H	3.3019760	-1.0733510	3.5195130
58	H	5.0537970	-1.2435610	3.3981620
59	H	4.1841950	-0.3105210	2.1764380
60	H	3.0320440	-5.1330110	-2.0328320
61	H	1.8558970	-5.7307000	-3.2193920
62	H	2.2114410	-3.9989980	-3.1253250
63	H	-1.2154950	-4.4394580	-1.6546800
64	H	-0.2911390	-3.6449930	-2.9472630
65	H	-0.5126280	-5.3956390	-2.9600330
66	H	-0.0407420	-5.9536680	0.0037900
67	H	0.5506100	-6.8716280	-1.3890400
68	H	1.6945250	-6.2875760	-0.1644500
69	H	-1.9172850	-1.5912600	0.5072450
70	H	-2.8700990	2.5485570	1.0022450
71	H	-0.4709510	3.1192890	0.7182670
72	C	-3.9862420	0.0610870	0.9037430
73	C	-5.0204520	0.6393820	0.1384430
74	C	-4.3013600	-0.8887700	1.8794310
75	C	-6.3678690	0.2706330	0.4070130
76	C	-4.7694770	1.5612610	-0.9405360
77	C	-5.6130670	-1.2538020	2.1374790
78	H	-3.4973590	-1.3198180	2.4632700
79	C	-7.4342590	0.8499930	-0.3447520
80	C	-6.6643900	-0.6780030	1.4201280
81	C	-5.7834030	2.1046590	-1.6550300
82	H	-3.7457030	1.8032710	-1.1899970
83	H	-5.8329980	-1.9804640	2.9104350
84	C	-7.1548230	1.7812630	-1.3767580
85	C	-8.7802680	0.4934110	-0.0665430
86	C	-8.0358830	-1.0226310	1.6807670
87	H	-5.5727580	2.7909530	-2.4667160
88	C	-8.2113230	2.3401380	-2.1024020
89	C	-9.8092760	1.0755710	-0.8125940
90	C	-9.0452480	-0.4621560	0.9750350
91	H	-8.2411000	-1.7457420	2.4611570
92	C	-9.5260820	1.9905140	-1.8201870
93	H	-7.9916010	3.0495620	-2.8913700
94	H	-10.8353820	0.8024170	-0.5965630
95	H	-10.0760690	-0.7265270	1.1789750
96	H	-10.3345080	2.4310410	-2.3895750

Table S16. TDDFT calculation data of **Py-PICR**

Wavelength (nm)	Oscillator strength	The main transition	coefficient
979.51	0.0348	βHOMO → βLUMO	0.97555
684.33	0.0367	αHOMO → αLUMO	0.94515
622.17	0.0591	βHOMO-3 → βLUMO βHOMO-1 → βLUMO	0.65467 0.60938
615.97	0.1026	βHOMO-3 → βLUMO βHOMO → βLUMO	-0.49811 0.73158
484.65	0.0265	αHOMO-1 → αLUMO+1 βHOMO-1 → βLUMO+1	-0.48404 0.53616
475.56	0.0101	αHOMO-1 → αLUMO βHOMO-6 → βLUMO	0.69675 0.52008
470.70	0.0604	αHOMO-1 → αLUMO βHOMO-1 → βLUMO	0.64910 -0.63695
418.81	0.0180	βHOMO-5 → βLUMO	0.76779

SCF Done: E(UM052X) = -2153.30009061 A.U.
S**2 before annihilation 1.0268, after 0.6252

Zero-point correction	=	0.801760 (Hartree/Particle)
Thermal correction to Energy	=	0.846094
Thermal correction to Enthalpy	=	0.847038
Thermal correction to Gibbs Free Energy	=	0.720586
Sum of electronic and zero-point Energies	=	-2152.498331
Sum of electronic and thermal Energies	=	-2152.453997
Sum of electronic and thermal Enthalpies	=	-2152.453053
Sum of electronic and thermal Free Energies	=	-2152.579505

Low frequencies --- -6.9642 -4.2194 -3.2484 -0.0007 -0.0005 0.0013

Low frequencies --- 8.2285 9.2073 14.1076

6. Transient Absorption Spectra and First-Order Kinetic Profiles

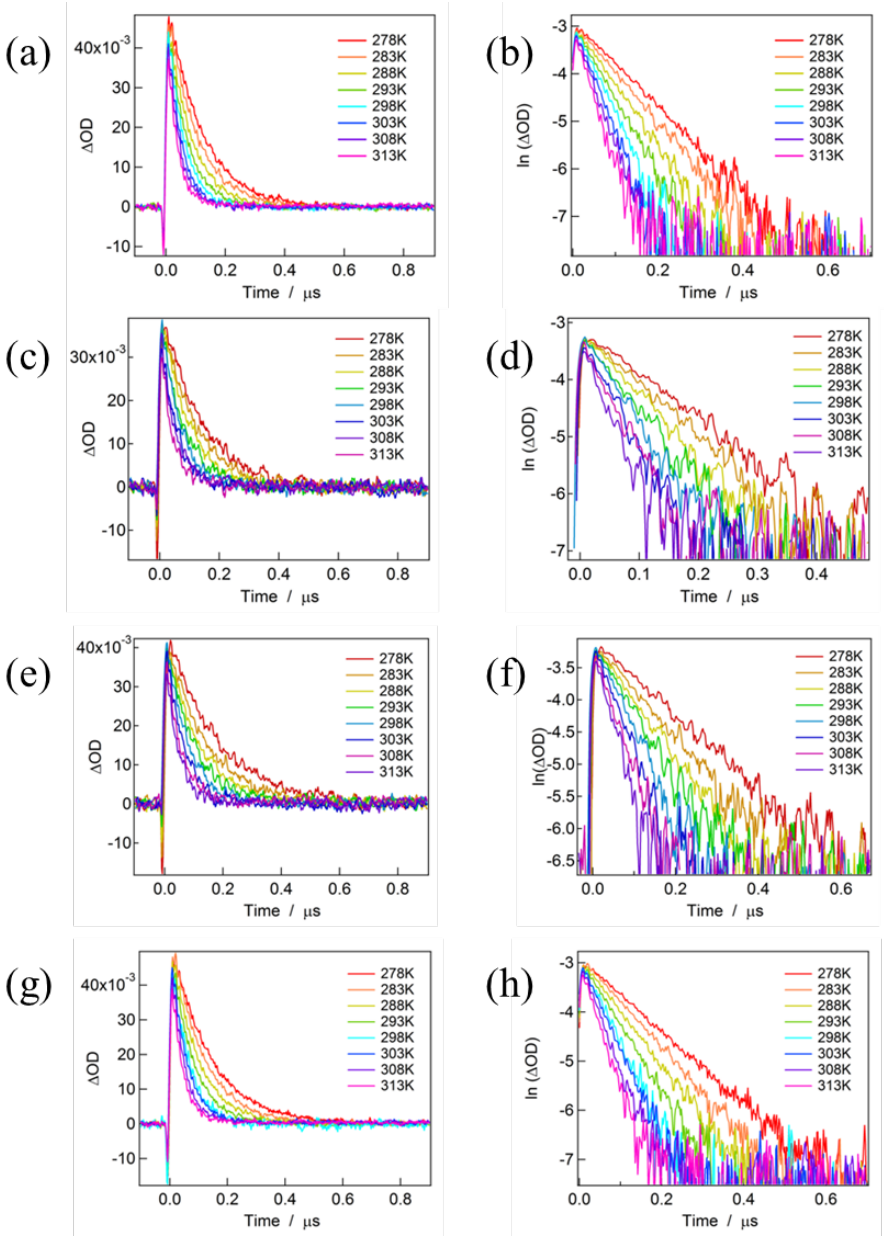

Figure S44. (a), (c), (e), (g) Transient absorption spectra and (b), (d), (f), (h) first-order kinetic profiles of the colored species generated from **Ph-PIC**, **Np-PIC**, **An-PIC** and **Py-PIC** in benzene. ($\lambda_{ex.}$ = 355 nm, $\lambda_{abs.}$ = 700 nm. [**Ph-PIC**] = 3.2 × 10^{-5} M, [**Np-PIC**] = 3.5 × 10^{-5} M, [**An-PIC**] = 3.1 × 10^{-5} M, [**Py-PIC**] = 3.3 × 10^{-5} M, power density 4.2 mJ).

7. Eyring Plot and Activation Parameters

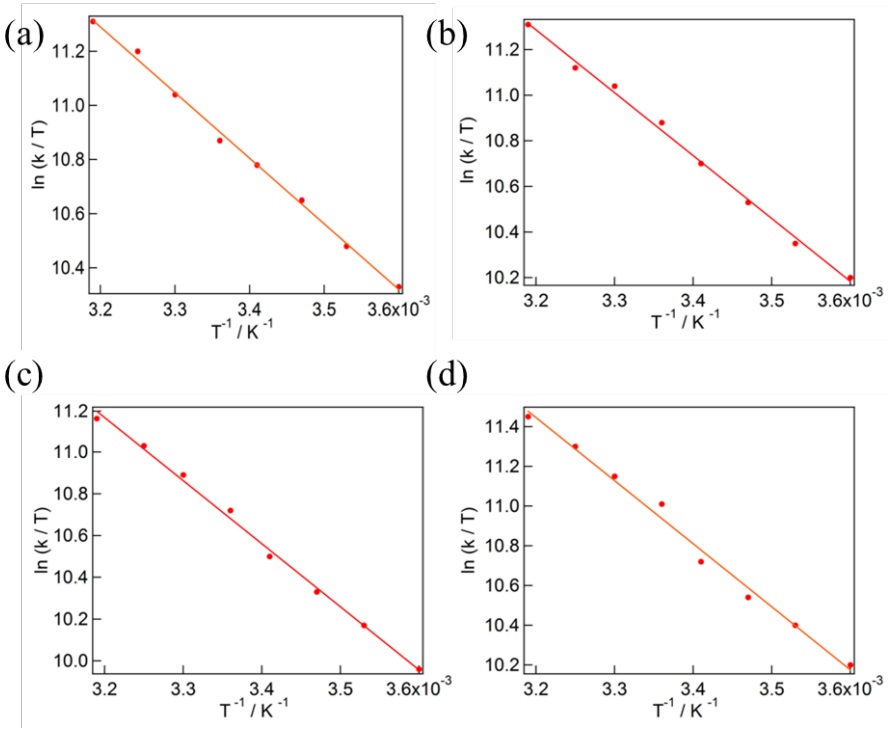

Figure S45. Eyring plot for the thermal back-reaction of colored species of **Ph-PIC**, **Np-PIC**, **An-PIC**, **Py-PIC** in benzene.

8. Dihedral Angle Between PIC Unit and π–Electron Conjugation Unit

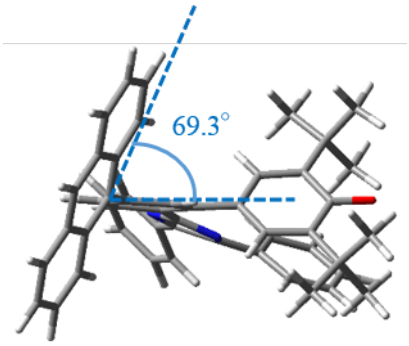

Figure S46. The calculated dihedral angle of **An-PIC** between PIC unit and the π–electron conjugation unit ((UM052X/6−31(d) level).

Table S17. The calculated dihedral angle between PIC unit and the π–electron conjugation unit ((UM052X/6−31(d) level).

Compound	Dihedral angle
Ph-PICR	37.0º
Np-PICR	55.5º
An-PICR	69.3º
Py-PICR	55.4º

9. Reference

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