Supplementary Information

CP-11-2025-004361

Dimer Formation of 7-Azaindole in Phosphonium-Based Ionic Liquids: Anion-Dependent Behavior

Faruk Hossain, Kotaro Takahashi, Maharoof Koyakkat and Hideaki Shirota*

Department of Chemistry, Chiba University,

1-33 Yayoi, Inage-ku, Chiba 263-8522, Japan

shirota@faculty.chiba-u.jp

1. Sample Preparation.

1.1. Trihexyltetradecylphosphonium bromide, $[P_{666,14}]Br$.

1-Bromotetradecane (6.61 mL, 24.34 mmol) was added to trihexylphosphine (7.00 mL, 20.28 mmol) at a nitrogen atmosphere in a flask equipped with a reflux condenser and a magnetic stirrer. The solution was then heated to 363-373 K in an oil bath for 2 days while stirring. The solution was allowed to cool to room temperature, and a highly viscous liquid was obtained. The liquid was then dissolved in acetonitrile and washed with hexane at least five times. The solution was removed with a rotatory evaporator. Subsequently, the highly viscous liquid was dried in vacuo at 313 K for more than 2 days. The yield was 94%. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.22-2.15 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.56-1.12 (m, 48H, $CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 1.03-0.69 (m, 12H, $PC_{13}H_{26}CH_3, P(C_5H_{10}CH_3)_3$). Elemental analysis: $C_{32}H_{68}BrP$. Calculated: C 68.17, H 12.16, N 0.00, Found: C 67.84, H 12.12, N 0.12.

1.2. Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide, $[P_{666,14}][NTf_2]$.

The synthesized $[P_{666,14}]Br$ (7.68 g, 13.62 mmol) was dissolved in a 1:1 (v/v) mixture of distilled water and acetone as a solvent. Lithium bis(trifluoromethylsulfonyl)amide, $Li[NTf_2]$ (4.69 g, 16.35 mmol) was dissolved in distilled water. The aqueous $Li[NTf_2]$ solution was added dropwise to the precursor solution. After that, the solution was stirred at room temperature for 2 days. Acetone was removed with a rotary evaporator. The remaining solution was dissolved in dichloromethane. The dichloromethane phase was washed with water several times, and then dichloromethane was removed with a rotary evaporator. The obtained viscous liquid was dried in vacuo at 313 K for more than 2 days. A colorless liquid was obtained. The yield was 92%. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.20-2.12 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.56-1.24 (m, 48H,

$CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 1.03-0.71 (m, 12H, $PC_{13}H_{26}CH_3$, $P(C_5H_{10}CH_3)_3$). Elemental analysis: $C_{34}H_{68}F_6NO_4PS_2$. Calculated: C 53.45, H 8.97, N 1.83, Found: C 53.38, H 8.95, N 1.81.

1.3. Trihexyltetradecylphosphonium bis(fluorosulfonyl)amide, $[P_{666,14}][NF_2]$.

$[P_{666,14}]Br$ (5.02 g, 8.91 mmol) was dissolved in a 1:1 (v/v) mixture of distilled water and acetone as a solvent. Lithium bis(fluoromethylsulfonyl)amide, $Li[NF_2]$ (2.05 g, 10.98 mmol) was dissolved in distilled water. The aqueous $Li[NF_2]$ solution was added dropwise to the aqueous precursor solution. After mixing, the solution was stirred at room temperature for 2 days. Acetone was removed with a rotary evaporator. The remaining solution was dissolved in dichloromethane. The dichloromethane phase was washed with water several times, and then dichloromethane was removed with a rotary evaporator. The obtained viscous solution was dried in vacuo at 313 K for more than 2 days. A clear colorless liquid was obtained. The yield was 95%. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.20-2.12 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.54-1.24 (m, 48H, $CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 0.89-0.84 (m, 12H, $PC_{13}H_{26}CH_3$, $P(C_5H_{10}CH_3)_3$). Elemental analysis: $C_{32}H_{68}F_2NO_4PS_2$. Calculated: C 57.89, H 10.32, N 2.11, Found: C 58.09, H 10.30, N 1.91.

1.4. Trihexyltetradecylphosphonium tetrafluoroborate, $[P_{666,14}][BF_4]$.

$[P_{666,14}]Br$ (5.58 g, 9.89 mmol) was dissolved in a 1:1 (v/v) mixture of distilled water and acetone as a solvent. Lithium tetrafluoroborate, $Li[BF_4]$ (1.11 g, 11.80 mmol) was dissolved in distilled water. The aqueous $Li[BF_4]$ solution was added dropwise to the precursor solution. The solution was then stirred at room temperature for 2 days. Acetone was removed with a rotary evaporator. The remaining solution was dissolved in dichloromethane. The dichloromethane phase was washed with water several times, and then dichloromethane was removed with a rotary

evaporator. The obtained viscous solution was dried in vacuo at 313 K for more than 2 days. A colorless liquid was obtained. The yield was 95%. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.32-2.12 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.56-1.24 (m, 48H, $CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 1.03-0.71 (m, 12H, $PC_{13}H_{26}CH_3, P(C_5H_{10}CH_3)_3$). Elemental analysis: $C_{32}H_{68}BF_4P$. Calculated: C 67.35, H 12.01, N 0.00, Found: C 67.46, H 12.01, N 0.01.

1.5. Trihexyltetradecylphosphonium trifluoromethanesulfonate, $[P_{666,14}][OTf]$.

$[P_{666,\ 14}]Br$ (5.00 g, 8.88 mmol) was dissolved in a 1:1 (v/v) mixture of distilled water and acetone as a solvent. Lithium trifluoromethanesulfonate, Li[OTf] (1.67 g, 10.72 mmol) was dissolved in distilled water. The aqueous Li[OTf] solution was added dropwise to the precursor solution. After mixing, the solution was stirred at room temperature for 2 days. Acetone was removed with a rotary evaporator. The remaining solution was dissolved in dichloromethane. The dichloromethane phase was washed with water several times, and then dichloromethane was removed with a rotary evaporator. The obtained viscous solution was dried in vacuo at 313 K for more than 2 days. A clear colorless liquid was obtained. The yield was 94%. ^{1}H NMR (400 MHz, DMSO-d_6): δ/ppm = 2.33-2.13 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.60-1.10 (m, 48H, $CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 0.91-0.84 (m, 12H, $PC_{13}H_{26}CH_3, P(C_5H_{10}CH_3)_3$). Elemental analysis: $C_{33}H_{68}F_3O_3PS$. Calculated: C 62.62, H 10.83, N 0.00, Found: C 62.78, H 10.79, N 0.05.

1.6. Trihexyltetradecylphosphonium bis(nonafluorobutanesulfonyl)amide $[P_{666,14}][NNf_2]$.

$[P_{666,\ 14}]Br$ (4.18 g, 7.42 mmol) was dissolved in a 1:1 (v/v) mixture of distilled water and acetone as a solvent. Lithium bis(nonafluorobutanesulfonyl)imide, $Li[NNf_2]$ (5.22 g, 8.90 mmol) was dissolved in distilled water. The aqueous $Li[NNf_2]$ solution was added dropwise to the

precursor solution. The solution was then stirred at room temperature for 2 days. Acetone was removed with a rotary evaporator. The remaining solution was dissolved in dichloromethane. The dichloromethane phase was washed with water several times, and then dichloromethane was removed with a rotary evaporator. The obtained viscous solution was dried in vacuo at 313 K for more than 2 days. A colorless liquid was obtained. The yield was 93%. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.32-2.08 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.60-1.23 (m, 48H, $CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 1.02-0.70 (m, 12H, $PC_{13}H_{26}CH_3, P(C_5H_{10}CH_3)_3$). Elemental analysis: $C_{40}H_{68}F_{18}NO_4PS_2$. Calculated: C 45.15, H 6.44, N 1.32, Found: C 45.25, H 6.33, N 1.15.

1.7. Trihexyltetradecylphosphonium dicyanamide, $[P_{666,14}][DCA]$.

Because the purity of $[P_{666,14}][DCA]$ (Iolitec) is not high enough (95%) and its ^{1}H NMR spectrum shows peaks due to impurities (Fig. S1), it was purified. The $[P_{666,14}][DCA]$ (Iolitec) was dissolved in dichloromethane, and the dichloromethane phase was washed with water several times. The dichloromethane was then removed with a rotary evaporator. Next, the residue was subjected to the activated charcoal treatment in acetonitrile. The IL was dried in vacuo at 313 K for more than 2 days. The purified $[P_{666,14}][DCA]$ was confirmed by ^{1}H NMR (>99%, Fig. S1). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.84-2.41 (m, 8H, $C_{13}H_{27}CH_2P(CH_2C_5H_{11})_3$), 1.04-1.62 (m, 48H, $CH_3(CH_2)_{12}CH_2P(CH_2(CH_2)_4CH_3)_3$), 1.01-0.57 (m, 12H, $PC_{13}H_{26}CH_3, P(C_5H_{10}CH_3)_3$).

1.8. (Acetylacetonato)(*N*,*N*,*N*',*N*'-tetramethylethylenediamine)copper(II) perchlorate ([Cu(acac)(tmen)][ClO_4]).

N, N, N`, N`,-Tetramethylethylenediamine (10 mmol) and acetylacetone (10 mmol) were added to aqueous ethanol (1:1 v/v) and afterward added to the aqueous ethanol (1:1) solution of

copper((II) perchlorate hexahydrate, $Cu(ClO_4)_2.6H_2O$ (10 mmol) at nitrogen atmosphere while stirring. Then aqueous solution of sodium carbonate (5.0 mmol) was added to neutralize the acetylacetone. After completion of the reaction, the crude product was recrystallized three times by ethanol. The product was dried in vacuo at 313 K for more than 2 days. Reddish violet crystals were obtained. Elemental analysis: $C_{11}H_{23}N_2O_6ClCu$. Calculated: C 34.92, H 6.13, N 7.41, Found: C 34.69, H 6.08, N 7.18.

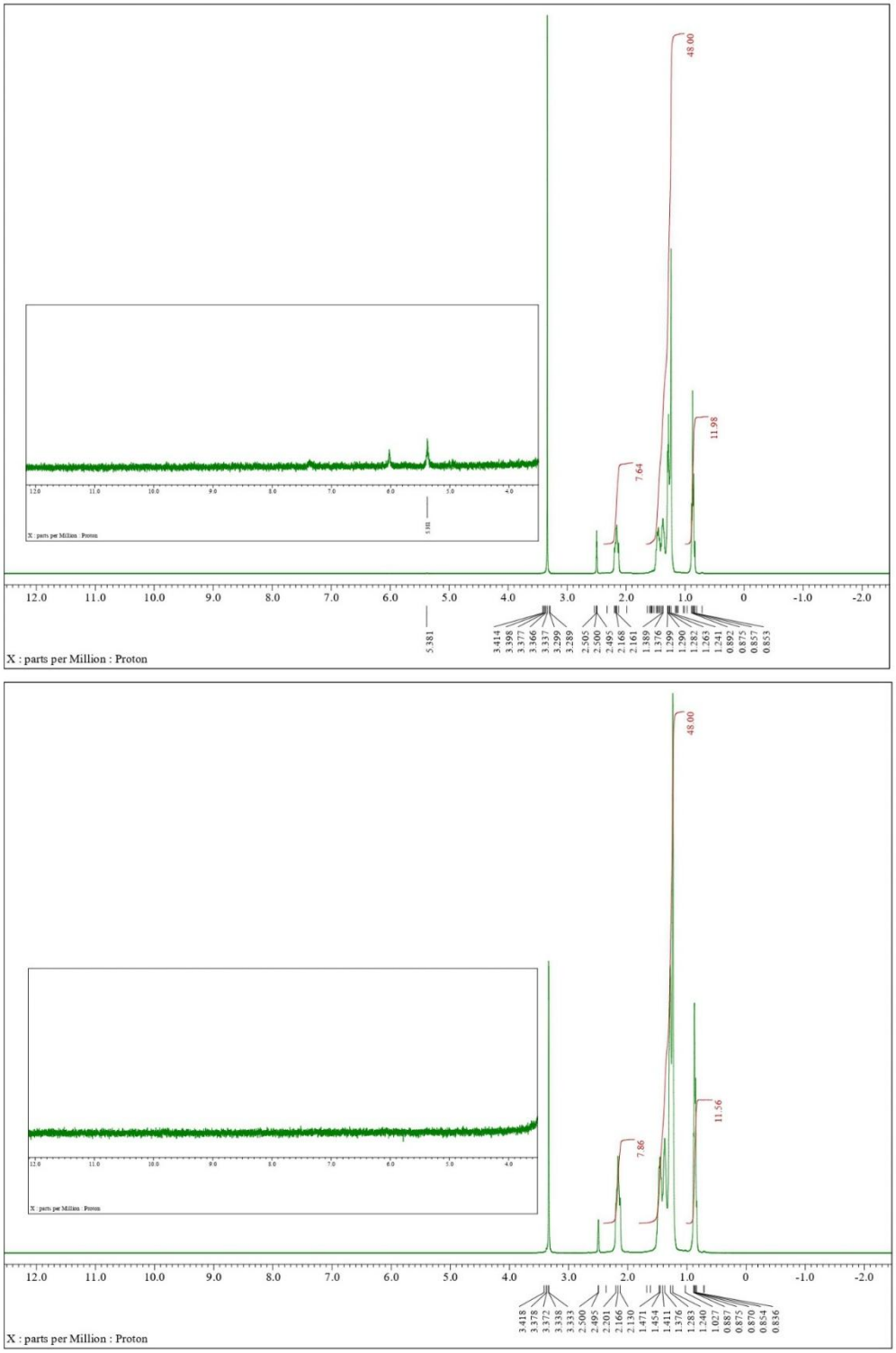

Fig. S1. ^{1}H NMR spectra of [$P_{666,14}$][DCA] (DMSO-d_6) before (upper) and after purification (lower). Peaks at 2.50 and 3.33 ppm are due to solvent and water, respectively.

2. Absorption Spectra of [Cu(acac)(tmen)][ClO_4] in Conventional Organic Solvents.

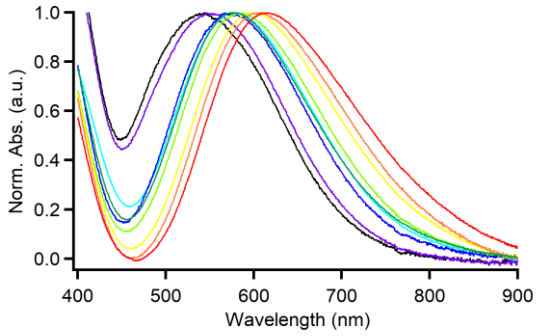

Fig. S2. Normalized absorption spectra of [Cu(acac)(tmen)][ClO_4] in various common organic solvents. Black: 1,2-dichloroethane; purple: dichloromethane; blue: anisole; light blue: acetonitrile; green: acetone; light green: ethylene glycol; yellow: formamide; orange: *N,N*-dimethylformamide; red: dimethyl sulfoxide.

Table S1. Absorption peak wavelength λ_{abs} and frequency ν_{abs} of [Cu(acac)(tmen)][ClO_4] in various common organic solvents and *DN* of the solvents.

Solvent	λ_{abs} (nm)	ν_{abs} (10^3 cm^{-1})	*DN*[1]
1,2-Dichloroethane	542.0	18.45	0
Dichloromethane	549.3	18.20	1
Anisole	578.9	17.27	9
Acetonitrile	577.8	17.30	14.1
Acetone	574.9	17.39	17.0
Ethylene glycol	585.4	17.08	20.0
Formamide	599.8	16.67	24.0
N, N-Dimethylformamide	606.0	16.50	26.6
Dimethyl sulfoxide	615.7	16.24	29.8

[1] S. Glikberg and Y. Marcus, *J. Sol. Chem.*, 1983, **12**, 255-270.

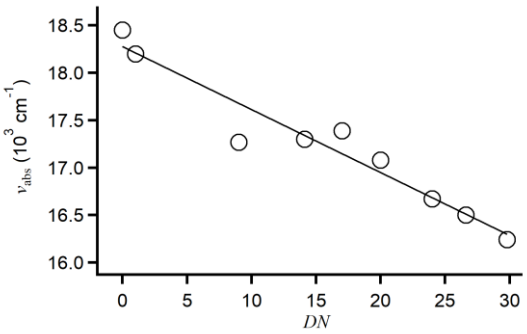

Fig. S3. Plots of ν_{abs} of [Cu(acac)(tmen)][ClO_4] vs. *DN*. The linear fit ($10^{-3}\nu_{abs}$ = 18.28 – 0.06632*DN*) is also shown.

3. Absorption Spectra of Betaine 30 in Conventional Organic Solvents.

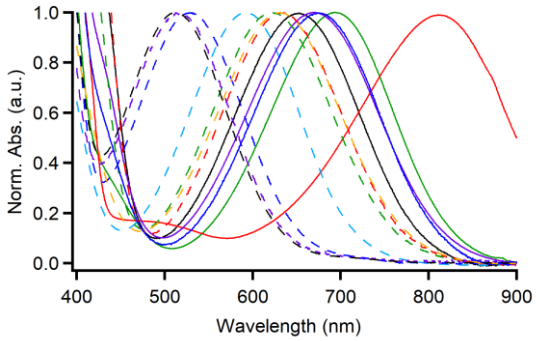

Fig. S4. Normalized absorption spectra of betaine 30 in various common organic solvents. Black dashed line: formamide; purple dashed line: methanol; blue dashed line: *N*-methylformamide; light blue dashed line: 2-propanol; green dashed line: acetonitrile; orange dashed line: *tert*-butanol; red dashed line: dimethyl sulfoxide; black solid line: *N,N*-dimethylformamide; purple solid line: methanol; blue solid line: 1,2-dichloroethane; green solid line: dichloromethane; red solid line: benzene.

Table S2. Absorption peak wavelength λ_{abs} and frequency ν_{abs} of betaine 30 in various common organic solvents and *AN* of the solvents.

Solvent	λ_{abs} (nm)	ν_{abs} (10^3 cm^{-1})	AN^2
Benzene	811.3	12.33	8.2
Acetone	669.7	14.93	12.5
N,N-Dimethylformamide	652.0	15.34	16.0
1,2-Dichloroethane	674.8	14.82	16.7
Acetonitrile	622.0	16.08	18.9
Dimethyl sulfoxide	633.1	15.80	19.3
Dichloromethane	693.6	14.42	20.4
tert-Butanol	630.8	15.85	27.1

N-Methylformamide	528.7	18.91	32.1
2-Propanol	592.4	16.88	33.5
Formamide	511.7	19.54	39.8
Methanol	515.7	19.39	41.3

[2] U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.* 1975, **106**, 1235-1257.

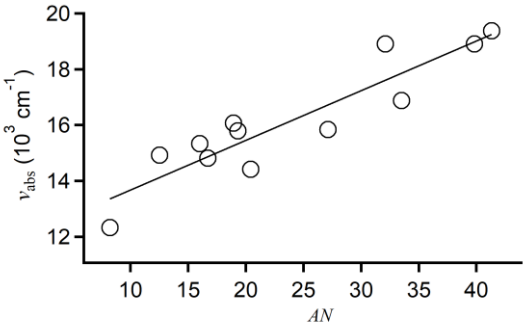

Fig. S5. Plots of ν_{abs} of betaine 30 vs. *AN*. The linear fit ($10^{-3}\nu_{abs}$ = 11.90 + 0.1780*AN*) is also shown.

4. Absorption Spectra of DENAN in Conventional Organic Solvents.

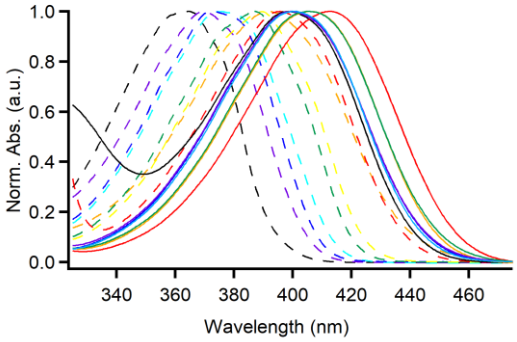

Fig. S6. Normalized absorption spectra of DENAN in various common organic solvents. Black broken line: hexane; purple broken line: triethylamine; blue broken line: diethyl ether; light blue dashed line: tetrachloroethylene; green broken line: tert-butanol; yellow broken line: toluene; red broken line: acetone; black solid line: 1,2-dichloroethane; purple solid line: anisole; blue solid line: acetonitrile; green solid line: formamide; orange solid line: *N,N*-ditmethylformamide; red solid line: dimethyl sulfoxide.

Table S3. Absorption peak wavelength λ_{abs} and frequency ν_{abs} of DENAN in various common organic solvents and π^* polarities of the solvents.

Solvent	λ_{abs} (nm)	ν_{abs} (10^3 cm^{-1})	π^* Polarity[3]
Hexane	364.4	27.44	-0.08
Triethylamine	369.9	27.03	0.14
Diethyl ether	372.9	26.82	0.27
Tetrachloroethylene	375.3	26.65	0.28
tert-Butaanol	386.7	25.86	0.41
Toluene	388.7	25.73	0.54
Benzene	391.8	25.52	0.59
Acetone	395.9	25.26	0.71

Anisole	399.8	25.01	0.73
Acetonitrile	400.4	24.98	0.75
1,2-Dichloroethane	398.9	25.07	0.81
Dichloromethane	400.5	24.97	0.82
N,N-Dimethylformamide	405.8	24.64	0.88
Formamide	405.4	24.67	0.97
Dimethyl sulfoxide	412.4	24.25	1.00

[3] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877-2887.

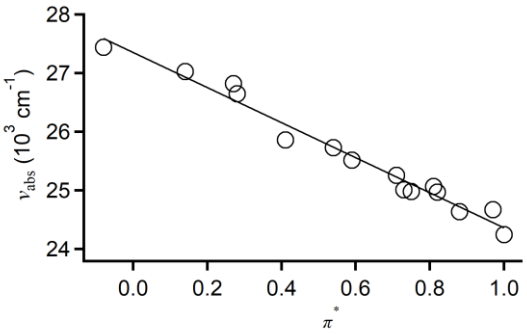

Fig. S7. Plots of ν_{abs} of DENAN vs. π^*. The linear fit ($10^{-3}\nu_{abs} = 27.35 - 2.992\pi^*$) is also shown.

5. Quantum Chemistry Calculations. Atom Coordinates of Anions, AI Monomer and Dimer, and AI–Anion Clusters at the ωB97XD/6-311++G(d,p) Level of Theory and Atomic Charges (Natural Bond Analysis) of Anions and AI Monomer and Dimer Optimized at the ωB97XD/6-311++G(d,p) Level of Theory.

Table S4. Atom coordinates and atomic charges of $[NF_2]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	7	0	0.000001	−0.000005	−0.835623	−1.18392
2	16	0	−1.391452	0.151216	−0.086768	2.42750
3	16	0	1.391451	−0.151217	−0.086761	2.42750
4	8	0	−2.416856	0.386840	−1.067227	−0.90562
5	8	0	2.416851	−0.386893	−1.067210	−0.90562
6	8	0	1.382251	−0.919568	1.132102	−0.90212
7	9	0	1.690946	1.380927	0.421529	−0.52780
8	9	0	−1.690928	−1.380913	0.421578	−0.52780
9	8	0	−1.382265	0.919612	1.132067	−0.90212
Rotational constants (GHz):			2.5251021	0.8790314	0.8621469	

Table S5. Atom coordinates and atomic charges of $[NTf_2]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	7	0	0.000001	0.000009	0.768581	−1.22794
2	16	0	−1.143672	−0.850444	0.053872	2.16306
3	16	0	1.143674	0.850447	0.053855	2.16306
4	8	0	−1.610896	−1.865005	0.976453	−0.92579
5	8	0	1.610905	1.865020	0.976420	−0.92579
6	8	0	0.923165	1.212020	−1.332091	−0.91867
7	8	0	−0.923168	−1.212036	−1.332070	−0.91867
8	6	0	2.559572	−0.372607	−0.005584	0.85079
9	6	0	−2.559574	0.372605	−0.005577	0.85079
10	9	0	2.912965	−0.766452	1.217598	−0.34975
11	9	0	3.625158	0.200038	−0.577530	−0.35717
12	9	0	2.239144	−1.451877	−0.714876	−0.34848
13	9	0	−2.239153	1.451865	−0.714887	−0.34848
14	9	0	−2.912962	0.766467	1.217601	−0.34975

15	9	0	−3.625161	−0.200051	−0.577509	−0.35717

Rotational constants (GHz): 1.0192428 0.3265457 0.3016831

Table S6. Atom coordinates and atomic charges of $[NNf_2]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	7	0	0.000000	1.458859	−0.000009	−1.18313
2	16	0	1.058948	0.728592	−0.972064	2.16171
3	16	0	−1.058948	0.728606	0.972057	2.16171
4	8	0	1.421395	1.660474	−2.034189	−0.90055
5	8	0	−1.421395	1.660502	2.034169	−0.90055
6	8	0	−0.811199	−0.672889	1.303878	−0.90773
7	8	0	0.811197	−0.672907	−1.303867	−0.90773
8	6	0	−2.613129	0.688543	−0.158183	0.49795
9	6	0	2.613128	0.688543	0.158177	0.49795
10	9	0	−3.095170	1.948687	−0.274712	−0.35178
11	9	0	−2.254843	0.256087	−1.384074	−0.34554
12	9	0	2.254841	0.256103	1.384073	−0.34554
13	9	0	3.095170	1.948687	0.274689	−0.35178
14	6	0	−3.757083	−0.233593	0.369922	0.64689
15	6	0	−5.154964	0.033233	−0.294798	0.63794
16	6	0	−6.208261	−1.105536	−0.087777	1.02545
17	6	0	3.757081	−0.233601	−0.369916	0.64689
18	6	0	5.154962	0.033234	0.294801	0.63794
19	6	0	6.208264	−1.105531	0.087784	1.02545
20	9	0	−3.432710	−1.525244	0.137968	−0.33669
21	9	0	−3.912981	−0.057665	1.701049	−0.33876
22	9	0	−5.690834	1.161577	0.219997	−0.33712
23	9	0	−5.013786	0.193123	−1.631263	−0.34296
24	9	0	−5.892101	−2.201791	−0.782178	−0.33317
25	9	0	−6.326710	−1.430499	1.205016	−0.33957
26	9	0	−7.405679	−0.673193	−0.521443	−0.34449
27	9	0	3.432707	−1.525248	−0.137945	−0.33669
28	9	0	5.013787	0.193132	1.631264	−0.34296
29	9	0	5.690827	1.161578	−0.220003	−0.33712
30	9	0	3.912979	−0.057690	−1.701045	−0.33876
31	9	0	6.326704	−1.430509	−1.205007	−0.33957
32	9	0	7.405684	−0.673175	0.521434	−0.34449

33	9	0	5.892118	−2.201780	0.782202	−0.33317
Rotational constants (GHz):			0.3591998	0.0437536	0.0432139	

Table S7. Atom coordinates and atomic charges of $[OTf]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	6	0	−0.945510	−0.000011	−0.000002	0.81385
2	16	0	0.928474	−0.000015	0.000000	2.24467
3	8	0	1.244110	0.807684	−1.178081	−0.98312
4	8	0	1.244128	0.616472	1.288473	−0.98312
5	8	0	1.244196	−1.424091	−0.110386	−0.98311
6	9	0	−1.445990	−0.537980	−1.124334	−0.36972
7	9	0	−1.445996	1.242675	0.096269	−0.36972
8	9	0	−1.446015	−0.704718	1.028060	−0.36972
Rotational constants (GHz):			2.7106339	1.5558311	1.5558165	

Table S8. Atom coordinates and atomic charges of $[BF_4]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	9	0	0.816968	0.816968	0.816968	−0.58400
2	9	0	−0.816968	−0.816968	0.816968	−0.58400
3	9	0	0.816968	−0.816968	−0.816968	−0.58400
4	9	0	−0.816968	0.816968	−0.816968	−0.58400
5	5	0	0.000000	0.000000	0.000000	1.33600
Rotational constants (GHz):			4.9819568	4.9819568	4.9819568	

Table S9. Atom coordinates and atomic charges of $[DCA]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	7	0	0.000000	0.000000	0.704672	−0.75848
2	6	0	0.000000	1.139900	0.064106	0.46859
3	6	0	0.000000	−1.139900	0.064106	0.46859

4	7	0	0.000000	2.208673	−0.407284	−0.58935
5	7	0	0.000000	−2.208673	−0.407284	−0.58935
Rotational constants (GHz):			43.2032951	3.0116949	2.8154316	

Table S10. Atom coordinates and atomic charges of Br^-.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	35	0	0.000000	0.000000	0.000000	−1

Table S11. Atom coordinates and atomic charges of AI monomer.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges
1	6	0	0.207503	−0.645106	0.000054	0.37831
2	6	0	0.233755	0.769931	−0.000036	−0.13514
3	6	0	−1.002330	1.416061	−0.000144	−0.14589
4	6	0	−2.139309	0.624866	−0.000126	−0.27891
5	6	0	−2.022302	−0.772303	−0.000020	0.05216
6	6	0	2.345336	0.009829	0.000060	0.00916
7	6	0	1.613457	1.160329	0.000090	−0.29471
8	1	0	−1.073771	2.498275	−0.000199	0.21080
9	1	0	−3.125648	1.072491	−0.000183	0.21359
10	1	0	−2.915835	−1.389453	0.000000	0.18644
11	1	0	3.415896	−0.124197	0.000058	0.20830
12	1	0	2.011385	2.162747	0.000091	0.22224
13	7	0	1.506497	−1.081847	0.000026	−0.56057
14	7	0	−0.864816	−1.425652	0.000065	−0.48051
15	1	0	1.779557	−2.049017	0.000333	0.41473
Rotational constants (GHz):			3.9693514	1.7111402	1.1956917	

Table S12. Atom coordinates and atomic charges of AI dimer.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Natural Charges

1	6	0	2.067321	0.182439	−0.000045	0.39428
2	6	0	3.429687	0.577393	0.000052	−0.13096
3	6	0	4.381460	−0.440292	0.000112	−0.13831
4	6	0	3.928180	−1.750595	0.000070	−0.28262
5	6	0	2.554053	−2.014350	−0.000026	0.06128
6	6	0	2.127016	2.398842	−0.000032	0.02333
7	6	0	3.436309	2.009375	0.000064	−0.30404
8	1	0	5.443141	−0.218311	0.000188	0.21143
9	1	0	4.624874	−2.579599	0.000112	0.21457
10	1	0	2.199351	−3.040644	−0.000058	0.18478
11	1	0	0.265811	1.314681	−0.000188	0.45585
12	1	0	1.711001	3.394697	−0.000062	0.20637
13	1	0	4.295342	2.661231	0.000129	0.22117
14	7	0	1.615154	−1.071487	−0.000081	−0.53319
15	7	0	1.295639	1.306234	−0.000099	−0.58395
16	6	0	−2.067321	−0.182442	−0.000049	0.39428
17	6	0	−3.429688	−0.577390	0.000053	−0.13096
18	6	0	−4.381457	0.440299	0.000117	−0.13831
19	6	0	−3.928172	1.750600	0.000073	−0.28262
20	6	0	−2.554044	2.014350	−0.000029	0.06128
21	6	0	−2.127026	−2.398845	−0.000034	0.02333
22	6	0	−3.436317	−2.009372	0.000063	−0.30404
23	1	0	−5.443139	0.218322	0.000196	0.21143
24	1	0	−4.624862	2.579607	0.000117	0.21457
25	1	0	−2.199337	3.040643	−0.000065	0.18478
26	1	0	−0.265817	−1.314691	−0.000180	0.45585
27	1	0	−1.711015	−3.394702	−0.000061	0.20637
28	1	0	−4.295353	−2.661224	0.000130	0.22117
29	7	0	−1.615148	1.071483	−0.000088	−0.53319
30	7	0	−1.295645	−1.306240	−0.000103	−0.58395
Rotational constants (GHz):			0.8828325	0.2476886	0.1934219	

Table S13. Atom coordinates of AI–$[NF_2]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−3.015656	0.203183	−0.182922
2	6	0	−3.625752	−0.980821	0.320213
3	6	0	−5.018462	−1.011550	0.330093

4	6	0	−5.693566	0.102843	−0.146754
5	6	0	−4.970306	1.207484	−0.616436
6	6	0	−1.395239	−1.203127	0.419076
7	6	0	−2.562046	−1.861056	0.697099
8	1	0	−5.559462	−1.877745	0.698160
9	1	0	−6.777161	0.132423	−0.161712
10	1	0	−5.500673	2.079940	−0.989878
11	1	0	−0.366733	−1.508540	0.551128
12	1	0	−2.646078	−2.850515	1.118658
13	7	0	−1.663962	0.033088	−0.107728
14	7	0	−3.643555	1.279659	−0.644175
15	1	0	−0.943892	0.690798	−0.388448
16	7	0	3.230878	0.450867	0.021778
17	16	0	2.978682	−1.111130	−0.126221
18	8	0	1.839797	−1.634507	0.590029
19	8	0	4.238859	−1.793087	−0.051494
20	9	0	2.542375	−1.253735	−1.695123
21	16	0	2.064033	1.514787	0.122689
22	8	0	2.622452	2.835280	0.102721
23	8	0	0.885558	1.232395	−0.670661
24	9	0	1.528722	1.327895	1.656514
Rotational constants (GHz):			0.7074995	0.1663638	0.1459952

Table S14. Atom coordinates of AI–$[NTf_2]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.587576	−0.487320	0.418379
2	6	0	4.188024	−1.200792	−0.657356
3	6	0	5.579241	−1.272631	−0.661688
4	6	0	6.262288	−0.647875	0.371777
5	6	0	5.548079	0.023839	1.373173
6	6	0	1.957958	−1.245167	−0.898497
7	6	0	3.118326	−1.673079	−1.482959
8	1	0	6.113072	−1.798693	−1.447001
9	1	0	7.345188	−0.671536	0.416973
10	1	0	6.084683	0.512889	2.182368
11	1	0	0.927310	−1.380366	−1.193120
12	1	0	3.195012	−2.252633	−2.389673

13	7	0	2.235433	−0.536663	0.241105
14	7	0	4.223077	0.115681	1.417435
15	1	0	1.522247	−0.105810	0.821486
16	7	0	−2.454327	0.793186	−0.089555
17	16	0	−2.531329	−0.669275	−0.721042
18	8	0	−1.267889	−1.358921	−0.915152
19	8	0	−3.495994	−0.664117	−1.798474
20	16	0	−1.230170	1.430721	0.697645
21	8	0	−1.712627	2.482999	1.562606
22	8	0	−0.249021	0.493118	1.228605
23	6	0	−0.304887	2.331168	−0.656646
24	6	0	−3.373355	−1.634562	0.642128
25	9	0	−1.055905	3.288153	−1.194402
26	9	0	0.059713	1.488702	−1.620281
27	9	0	0.793344	2.892288	−0.149757
28	9	0	−4.580053	−1.138758	0.905525
29	9	0	−2.654487	−1.609626	1.760413
30	9	0	−3.519063	−2.907264	0.264043
Rotational constants (GHz):			0.3329581	0.1207215	0.1047587

Table S15. Atom coordinates of AI–[NNf_2]$^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.912404	2.779110	0.491908
2	6	0	−3.147182	3.529723	−0.693317
3	6	0	−4.334511	4.255784	−0.748826
4	6	0	−5.186149	4.186083	0.344184
5	6	0	−4.833831	3.406656	1.454124
6	6	0	−1.200452	2.432734	−0.892188
7	6	0	−2.031514	3.289900	−1.558176
8	1	0	−4.590218	4.851327	−1.619568
9	1	0	−6.125906	4.726384	0.351982
10	1	0	−5.502816	3.352477	2.309228
11	1	0	−0.271052	1.973902	−1.196482
12	1	0	−1.870896	3.687199	−2.548197
13	7	0	−1.718195	2.135329	0.341987
14	7	0	−3.710451	2.703346	1.551059
15	1	0	−1.313746	1.449087	0.970060

16	7	0	0.924178	−1.935143	−0.084868
17	16	0	1.854394	−0.952310	−0.930718
18	8	0	1.319832	0.369216	−1.199266
19	8	0	2.455388	−1.700435	−2.013038
20	16	0	−0.272395	−1.503296	0.870190
21	8	0	−0.515604	−2.545701	1.841135
22	8	0	−0.242828	−0.120120	1.323842
23	6	0	3.282305	−0.660143	0.268767
24	6	0	−1.744375	−1.615344	−0.305655
25	9	0	2.869734	0.181396	1.230250
26	9	0	3.620742	−1.824979	0.837989
27	9	0	−1.604775	−0.662374	−1.241069
28	9	0	−1.718323	−2.809650	−0.910525
29	6	0	4.553297	−0.064307	−0.410612
30	6	0	−3.130442	−1.449613	0.395044
31	9	0	4.204667	0.884220	−1.292260
32	9	0	5.204795	−1.042022	−1.063167
33	9	0	−3.469670	−2.620239	0.964307
34	9	0	−3.059180	−0.515304	1.351126
35	6	0	−4.275467	−1.034406	−0.584935
36	6	0	−5.714913	−1.199166	−0.005181
37	6	0	5.553671	0.586342	0.601886
38	6	0	6.988502	0.814870	0.032313
39	9	0	5.085753	1.783277	0.984291
40	9	0	5.686024	−0.194964	1.688368
41	9	0	7.680980	1.561986	0.895223
42	9	0	7.636846	−0.333306	−0.128381
43	9	0	6.947155	1.454097	−1.133344
44	9	0	−4.213290	−1.790682	−1.698467
45	9	0	−4.130025	0.250411	−0.924927
46	9	0	−6.582979	−0.631902	−0.845440
47	9	0	−6.043191	−2.483414	0.116568
48	9	0	−5.830773	−0.611933	1.179100
Rotational constants (GHz):			0.1587608	0.0376345	0.0336030

Table S16. Atom coordinates of AI–[OTf]⁻.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	−2.573852	−0.267716	0.202399
2	6	0	−3.328474	0.861056	−0.232311
3	6	0	−4.686467	0.656527	−0.465840
4	6	0	−5.193992	−0.618206	−0.259264
5	6	0	−4.342247	−1.644840	0.171023
6	6	0	−1.190936	1.468730	0.066195
7	6	0	−2.413530	1.957979	−0.309774
8	1	0	−5.328320	1.466501	−0.798812
9	1	0	−6.243499	−0.833367	−0.426239
10	1	0	−4.741386	−2.643376	0.332577
11	1	0	−0.226252	1.950664	0.149287
12	1	0	−2.628910	2.973378	−0.604637
13	7	0	−1.283692	0.138298	0.374335
14	7	0	−3.043202	−1.495066	0.406302
15	1	0	−0.478312	−0.419745	0.671950
16	8	0	1.972512	1.514079	0.726884
17	8	0	1.276732	−0.821249	1.099608
18	16	0	2.387114	0.116109	0.859844
19	8	0	3.586516	−0.128722	1.646903
20	6	0	2.904082	−0.326665	−0.880145
21	9	0	1.889233	−0.166808	−1.740294
22	9	0	3.308457	−1.599667	−0.966849
23	9	0	3.914260	0.445533	−1.302517
Rotational constants (GHz):			1.0023976	0.1852480	0.1814126

Table S17. Atom coordinates of AI–$[BF_4]^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.626009	−0.283241	−0.000780
2	6	0	2.424946	0.897386	0.000177
3	6	0	3.806824	0.721384	0.001094
4	6	0	4.293727	−0.577774	0.001028
5	6	0	3.398105	−1.656086	0.000020
6	6	0	0.257128	1.468282	−0.001166
7	6	0	1.517706	2.003327	−0.000025
8	1	0	4.482179	1.571554	0.001899
9	1	0	5.360322	−0.772727	0.001750
10	1	0	3.780889	−2.673909	−0.000037

11	1	0	−0.714926	1.938586	−0.001752
12	1	0	1.763169	3.054128	0.000596
13	7	0	0.317605	0.101579	−0.001578
14	7	0	2.075130	−1.534848	−0.000896
15	1	0	−0.511295	−0.497552	−0.002250
16	9	0	−2.192147	−1.093796	−0.002418
17	9	0	−4.081266	−0.415974	−1.147335
18	9	0	−2.801859	1.130689	−0.008214
19	9	0	−4.067292	−0.406115	1.159381
20	5	0	−3.314617	−0.192024	0.000461
Rotational constants (GHz):			1.7487489	0.2758877	0.2502213

Table S18. Atom coordinates of AI–[DCA]⁻.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.286489	0.253142	−0.000188
2	6	0	−2.209982	−0.831346	−0.000172
3	6	0	−3.564280	−0.503504	−0.000180
4	6	0	−3.903729	0.841190	−0.000193
5	6	0	−2.894052	1.814105	−0.000193
6	6	0	−0.119643	−1.639488	−0.000127
7	6	0	−1.431197	−2.031323	−0.000195
8	1	0	−4.329649	−1.273504	−0.000189
9	1	0	−4.942036	1.153119	−0.000205
10	1	0	−3.161391	2.867983	−0.000194
11	1	0	0.785053	−2.230883	−0.000101
12	1	0	−1.790390	−3.048733	−0.000225
13	7	0	−0.027550	−0.272500	−0.000068
14	7	0	−1.593118	1.546909	−0.000188
15	1	0	0.865689	0.232124	−0.000013
16	7	0	2.825100	0.311470	0.000114
17	6	0	3.262039	−0.926160	0.000614
18	6	0	3.670910	1.318878	−0.000156
19	7	0	3.513099	−2.065151	0.001092
20	7	0	4.344078	2.268835	−0.000141
Rotational constants (GHz):			1.3793695	0.3437501	0.2751744

Table S19. Atom coordinates of AI–[Br]$^{-}$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.262264	−0.233842	0.000095
2	6	0	−2.136294	0.894555	−0.000014
3	6	0	−3.504566	0.632167	−0.000113
4	6	0	−3.908764	−0.694792	−0.000092
5	6	0	−2.946190	−1.714383	0.000013
6	6	0	−0.011167	1.597553	0.000058
7	6	0	−1.302473	2.056422	0.000041
8	1	0	−4.232000	1.438429	−0.000169
9	1	0	−4.960984	−0.956802	−0.000150
10	1	0	−3.264641	−2.754317	0.000025
11	1	0	0.928474	2.130076	0.000049
12	1	0	−1.614387	3.089566	0.000044
13	7	0	0.017567	0.233577	0.000083
14	7	0	−1.633996	−1.511247	0.000109
15	1	0	0.909766	−0.283780	0.000024
16	35	0	3.256545	−0.255587	−0.000031
Rotational constants (GHz):			2.5256059	0.3478498	0.3057404

6. DSC Charts.

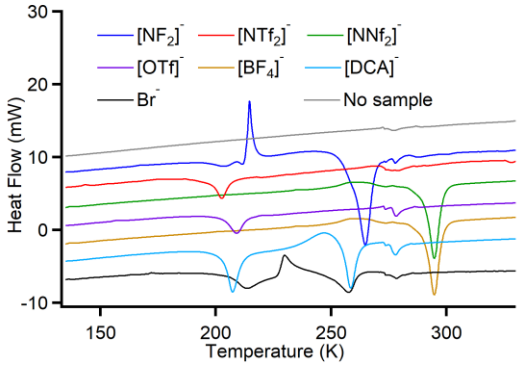

Figure S8. DSC charts of $[P_{666,14}][NF_2]$ (blue), $[P_{666,14}][NTf_2]$ (red), $[P_{666,14}][NNf_2]$ (green), $[P_{666,14}][OTf]$ (purple), $[P_{666,14}][BF_4]$ (brown), $[P_{666,14}][DCA]$ (light blue), $[P_{666,14}]Br$ (black), and no sample (gray). The DSC trace for the no-sample (vacancy) shows some artifact peaks at ~278 K. The peaks at ~278 K for the ILs are assigned to an artifact.

7. Absorption Spectral Data of Solvatochromic Dyes in Phosphonium-Based ILs.

Table S13. Absorption peak wavelength λ_{abs} and frequency ν_{abs} of [Cu(acac)(tmen)][ClO_4], betaine 30, and DENAN in the ILs.

	[Cu(acac)(tmen)][ClO_4]		betaine 30		DENAN	
	λ_{abs} (nm)	ν_{abs} (10^3 cm^{-1})	λ_{abs} (nm)	ν_{abs} (10^3 cm^{-1})	λ_{abs} (nm)	ν_{abs} (10^3 cm^{-1})
[$P_{666,14}$][NF_2]	633.7	15.78	639.0	15.65	405.8	24.64
[$P_{666,14}$][NTf_2]	636.1	15.72	631.1	15.85	404.3	24.73
[$P_{666,14}$][NNf_2]	636.5	15.71	616.4	16.22	404.5	24.72
[$P_{666,14}$][OTf]	640.9	15.60	640.4	15.62	404.6	24.72
[$P_{666,14}$][BF_4]	662.2	15.10	635.7	15.73	404.0	24.75
[$P_{666,14}$][DCA]	646.8	15.46	645.4	15.49	405.8	24.64
[$P_{666,14}$]Br	670.5	14.91	655.4	15.26	405.4	24.67