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

Electronic Supplementary Information

Reliable experimental method for determination of photoacidity revealed by quantum chemical calculations

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Table S1. Various pK_a^* values of coumarin 183 depending on experimental methods.

Method		**pK_a^***
Fluorescence titration		1.20
Time-resolved experiments		−1.84
Förster cycle	Maximum absorption wavelength, $\lambda_{abs, max}$	−5.90
	Maximum emission wavelength, $\lambda_{emi, max}$	0.95
	Average of maximum absorption and emission wavelengths, $\lambda_{avg, max}$	−2.47
	Average of the first moments of absorption and emission spectra, $\lambda_{avg, moment}$	0.79
	Cross point	−1.85
	Optical bandgap	−1.50

Table S2. Experimentally-determined pK_a and pK_a^* values of photoacids reported in the literature.

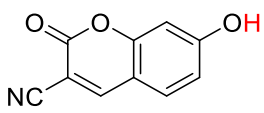
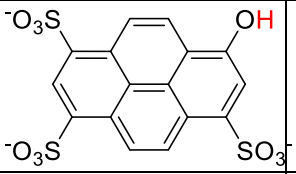
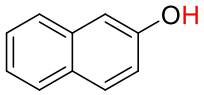
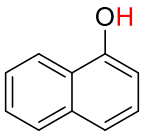
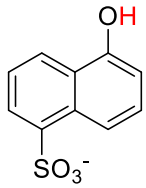
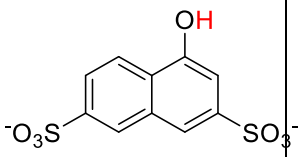
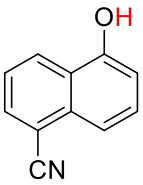
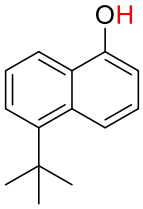
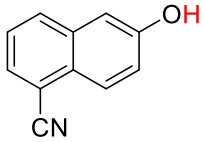
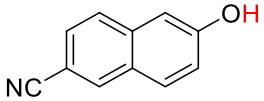
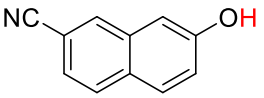
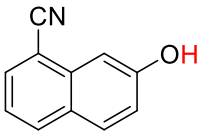
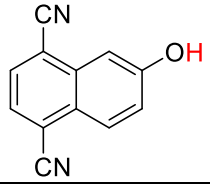
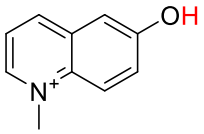
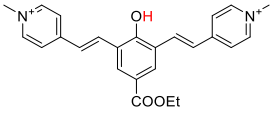
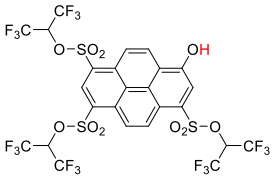
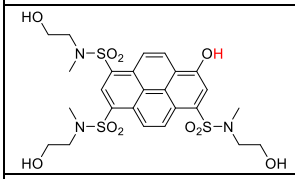
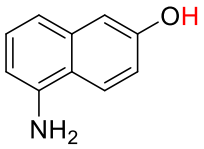
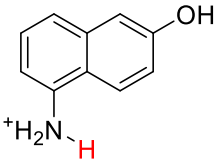
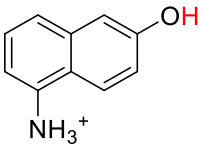
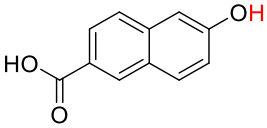
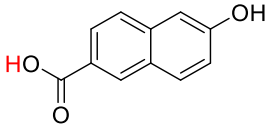
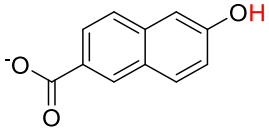
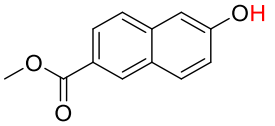
Photoacids	Ground state pK_a	Fluorescence titration	Förster cycle	Time-resolved experiment
Coumarin 183	5.5[1-3]	1.20[1-3]	0.79[1-3]	–1.84[1-3]
HPTS	7.7[4]	1.42[5]		1.41[a4]
2-naphthol	9.45[6]	2.80[7]	2.80[7]	2.90[8]
1-naphthol	9.4[9]		1.86[10]	0.43[11] –0.20[a12]
5-sulfonate-1-naphthol	8.4[13]		–0.70[13]	
3,6-disulfonate-1-naphthol	8.6[13]		–2.60[13]	
5-cyano-1-naphthol	8.05[14]		–2.80[14]	
5-tButyl-1-naphthol	9.8[13]		1.00[13]	
5-cyano-2-naphthol	8.75[6]	1.70[6]	–1.20[6]	–0.75[a15]
6-cyano-2-naphthol	8.4[6]	0.50[6]	0.20[6]	–0.37[a15]
7-cyano-2-naphthol	8.75[6]	2.00[6]	–1.30[6]	–0.21[a15]
8-cyano-2-naphthol	8.35[6]	0.70[6]	–0.40[6]	–0.76[a15]
5,8-dicyano-2-naphthol	7.8[6]		–4.50[15]	
MHQ				–0.13[a16]
QCy9	4.3[17]		–8.50[17]	
HPTS-derivative 1a	4.4[18]		–3.90[18]	
HPTS-derivative 1b	5.7[18]		–0.90[18]	
5-amino-2-naphthol (N-A)	9.5[19]		10.24[19]	9.50[19]
5-amino-2-naphthol (C-N)	4.0[19]		–4.21[19]	
5-amino-2-naphthol (C-Z)				1.10[19]
6-Carboxy-2-naphthol (OH)	8.9[20]		1.40[20]	
6-Carboxy-2-naphthol (COOH)	4.3[20]		7.80[20]	
6-Carboxylate-2-naphthol	9.5[20]		2.50[20]	
6-Methylester-2-naphthol	8.6[20]		–1.20[20]	
2-naphthoic acid	4.2[20]		6.60[20]	
QCy7	4.5[21]		–5.70[21]	
SulfoQcy7	4.5[21]		–4.60[21]	
Tetrasulfo-QCy7	4.5[21]		–4.85[21]	
7-hydroxy-4-methylflavylium	4.45[22]			–0.70[22]
BCyP	6.5[23]		–4.56[23]	
DPI	12.8[24]		7.00[24]	
protonated 6-Aminochrysene	3.15[25]	–3.40[25]	–3.26[25]	
6-sulfonate-2-naphthol	9.1[26]			1.95[26]

Photoacids	Ground state pK_a	Fluorescence titration	Förster cycle	Time-resolved experiment
naphthalen-1-aminium	3.9[27]			–1.00[27]
naphthalen-2-aminium	4.1[27]			–0.80[27]
CBCyP	6.0[28]		–7.50[28]	
3HF	9.6[29]	–1.85[29]	0.54[29]	
Protonated DEA3HF	3.25[29]			
DEA3HF	10.54[29]	–1.89[29]	1.23[29]	
F3HF	10.33[29]	–2.25[29]	–2.42[29]	
Protonated 1H-phenanthro[9,10-d]imidazole	4.65[30]	2.20[30]	2.26[30]	
1H-phenanthro[9,10-d]imidazole	11.86[30]	11.66[30]	7.95[30]	
OG488 (N-A)	3.61[31]			3.14[31]
OG488 (C-N)	1.02[31]			–1.79[31]
EG-dHONI	8.8[32]		–1.20[32]	
COOH-dHONI	8.8[32]		–1.40[32]	
EG-SHONI	8.0[32]		–1.90[32]	
HCD	5.4[33]		–2.43[33]	
o-cyanophenol	6.97[34]		0.50[34]	0.66[34]
m-cyanophenol	8.4[34]		2.20[34]	1.89[34]
p-cyanophenol	7.74[34]		3.20[34]	3.33[34]
3,4-dicyanophenol	6.5[35]		–0.90[35]	
phenol	10.0[36]	3.70[37]	4.00[36]	
m-fluorophenol	9.21[36]		3.80[36]	
p-fluorophenol	9.91[36]		4.40[36]	
m-chlorophenol	9.13[36]		3.00[36]	
p-chlorophenol	9.42[36]	2.60[37]	3.20[36]	
m-bromophenol	9.03[36]		2.80[36]	
p-bromophenol	9.36[36]		3.10[36]	
m-methylphenol	10.09[36]		4.00[36]	
p-methylphenol	10.26[36]	3.71[37]	4.30[36]	
m-ethylphenol	10.07[36]		4.10[36]	
p-ethylphenol	10.21[36]		4.30[36]	
p-sulfonate-phenol	9.03[36]		2.40[36]	
p-trimethylaminophenol	8.35[36]		1.70[36]	
5-bromo-8-hydroxyquinoline		–8.60[38]		
5-sulfonate-8-hydroxyquinoline		–9.30[38]		
5-thiocyano-8-hydroxyquinoline		–8.95[38]		

Photoacids	Ground state pK_a	Fluorescence titration	Förster cycle	Time-resolved experiment
7-fluoro-8-hydroxyquinoline		–9.40[38]		
7-chloro-8-hydroxyquinoline		–9.20[38]		
7-bromo-8-hydroxyquinoline		–8.65[38]		
7-sulfonate-8-hydroxyquinoline		–9.15[38]		
7-chloro-5-fluoro-8-hydroxyquinoline		–8.80[38]		
5,7-dichloro-8-hydroxyquinoline		–8.75[38]		
5-bromo-7-chloro-8-hydroxyquinoline		–8.40[38]		
7-bromo-5-fluoro-8-hydroxyquinoline		–8.60[38]		
7-bromo-5-chloro-8-hydroxyquinoline		–8.55[38]		
5,7-dibromo-8-hydroxyquinoline		–8.20[38]		
5,7-disulfonate-8-hydroxyquinoline		–9.60[38]		

[a] pK_a^* values are determined by the Debye-Smoluchowski equation. These values are not included in Figure 2c.

Table S3. Molecular structures of photoacids. (Proton in red is labile.)

Coumarin 183	HPTS	2-naphthol	1-naphthol
			
5-sulfonate-1-naphthol	3,6-disulfonate-1-naphthol	5-cyano-1-naphthol	5-tButyl-1-naphthol
			
5-cyano-2-naphthol	6-cyano-2-naphthol	7-cyano-2-naphthol	8-cyano-2-naphthol
			
5,8-dicyano-2-naphthol	MHQ	QCy9	HPTS-derivative 1a
			
HPTS-derivative 1b	5-amino-2-naphthol (N-A)	5-amino-2-naphthol (C-N)	5-amino-2-naphthol (C-Z)
			
6-Carboxy-2-naphthol (OH)	6-Carboxy-2-naphthol (COOH)	6-Carboxylate-2-naphthol	6-Methylester-2-naphthol
			
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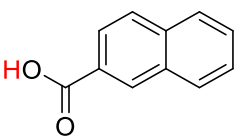
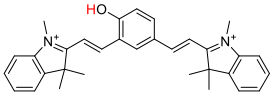
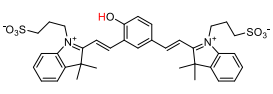
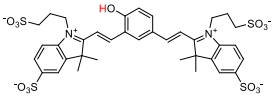
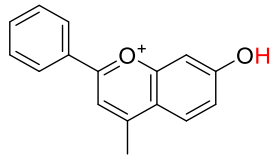
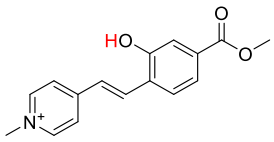
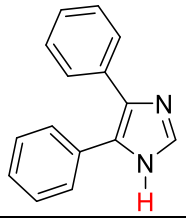
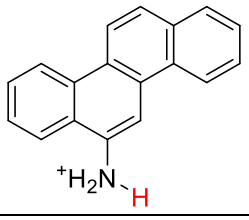
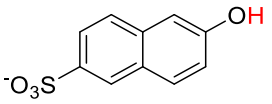
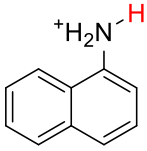
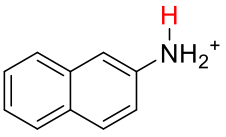
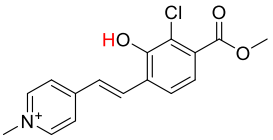
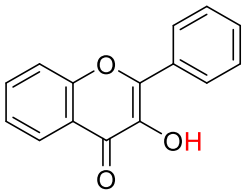
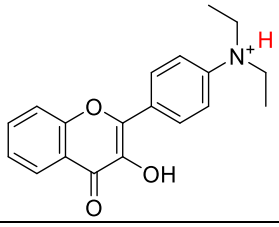
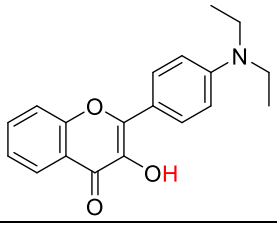
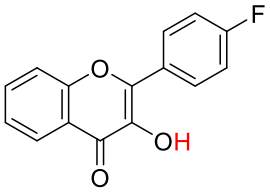
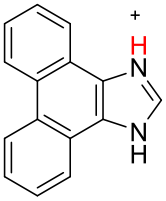
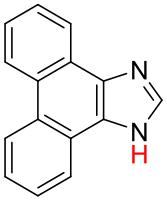
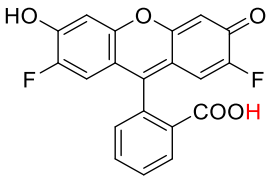
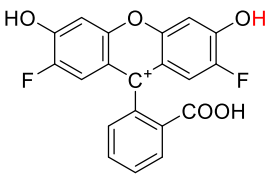
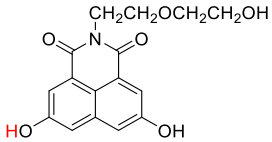
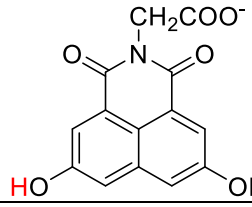
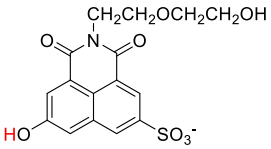
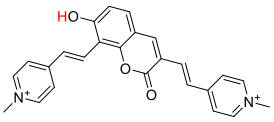
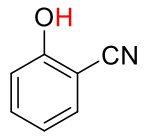
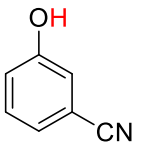
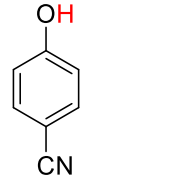
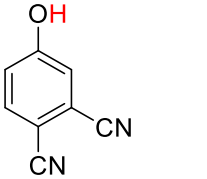
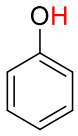
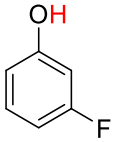
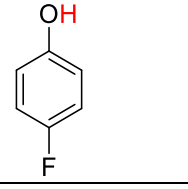
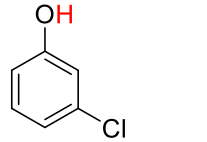
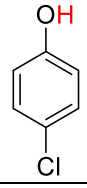
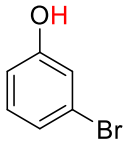
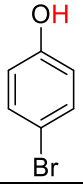
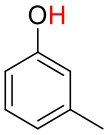
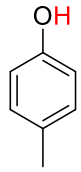
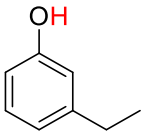
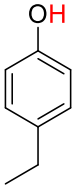
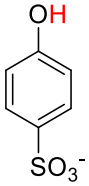
			
7-hydroxy-4-methylflavylium	BCyP	DPI	protonated 6-Aminochrysene

			
6-sulfonate-2-naphthol	naphthalen-1-aminium	naphthalen-2-aminium	CBCyP
			
3HF	Protonated DEA3HF	DEA3HF	F3HF
			
Protonated 1H-phenanthro[9,10-d]imidazole	1H-phenanthro[9,10-d]imidazole	OG488 (N-A)	OG488 (C-N)
			
EG-dHONI	COOH-dHONI	EG-SHONI	HCD
			
o-cyanophenol	m-cyanophenol	p-cyanophenol	3,4-dicyanophenol
			
phenol	m-fluorophenol	p-fluorophenol	m-chlorophenol
			
p-chlorophenol	m-bromophenol	p-bromophenol	m-methylphenol

			
p-methylphenol	m-ethylphenol	p-ethylphenol	p-sulfonate-phenol
			
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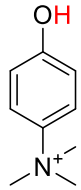
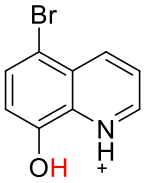
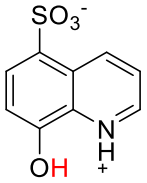
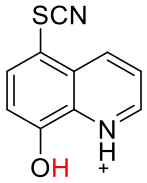
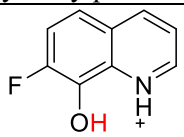
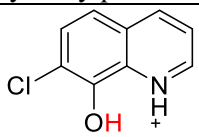
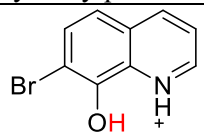
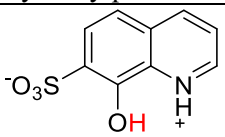
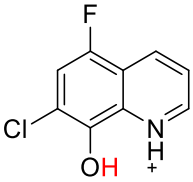
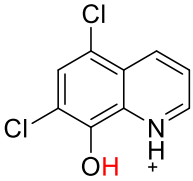
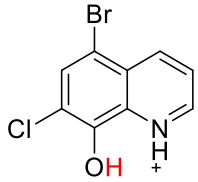
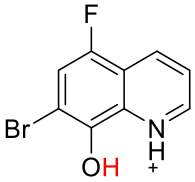
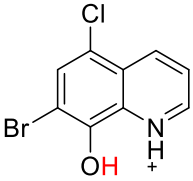
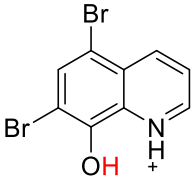
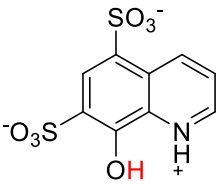
			
7-fluoro-8-hydroxyquinoline	7-chloro-8-hydroxyquinoline	7-bromo-8-hydroxyquinoline	7-sulfonate-8-hydroxyquinoline
			
7-chloro-5-fluoro-8-hydroxyquinoline	5,7-dichloro-8-hydroxyquinoline	5-bromo-7-chloro-8-hydroxyquinoline	7-bromo-5-fluoro-8-hydroxyquinoline
			
7-bromo-5-chloro-8-hydroxyquinoline	5,7-dibromo-8-hydroxyquinoline	5,7-disulfonate-8-hydroxyquinoline	
			

Table S4. DFT-calculated ΔG and pK_a values of photoacids in the ground state, $pK_a(\text{Calc.}) = k\Delta G + C$.

Photoacids	ΔG (kJ/mol)	pK_a (Expt.)	pK_a (Calc.)	Error
Coumarin 183	1170.1	5.5[1-3]	5.94	0.44
HPTS	1182.6	7.7[4]	7.10	-0.60
2-naphthol	1208.6	9.45[6]	9.52	0.07
1-naphthol	1202.7	9.4[9]	8.97	-0.43
5-sulfonate-1-naphthol	1190.3	8.4[13]	7.82	-0.58
3,6-disulfonate-1-naphthol	1188.1	8.6[13]	7.62	-0.98
5-cyano-1-naphthol	1194.6	8.05[14]	8.21	0.16
5-tButyl-1-naphthol	1203.5	9.8[13]	9.04	-0.76
5-cyano-2-naphthol	1202.4	8.75[6]	8.94	0.19
6-cyano-2-naphthol	1197.7	8.4[6]	8.50	0.10
7-cyano-2-naphthol	1202.4	8.75[6]	8.94	0.19
8-cyano-2-naphthol	1198.1	8.35[6]	8.54	0.19
5,8-dicyano-2-naphthol	1191.9	7.8[6]	7.97	0.17
MHQ	1189.2		7.71	
QCy9	1157.4	4.3[17]	4.77	0.47
HPTS-derivative 1a	1157.1	4.4[18]	4.75	0.35
HPTS-derivative 1b	1148.5	5.7[18]	3.95	-1.75
5-amino-2-naphthol (N-A)	1210.7	9.5[19]	9.70	0.20
5-amino-2-naphthol (C-N)	1145.2	4.0[19]	3.64	-0.36
5-amino-2-naphthol (C-Z)	1201.7		8.87	
6-Carboxy-2-naphthol (OH)	1199.8	8.9[20]	8.69	-0.21
6-Carboxy-2-naphthol (COOH)	1160.7	4.3[20]	5.08	0.78
6-Carboxylate-2-naphthol	1204.7	9.5[20]	9.15	-0.35
6-Methylester-2-naphthol	1200.4	8.6[20]	8.76	0.16
2-naphthoic acid	1158.6	4.2[20]	4.88	0.68
QCy7	1158.4	4.5[21]	4.87	0.37
SulfoQcy7	1119.9	4.5[21]	1.30	-3.20
Tetrasulfo-QCy7	1155.2	4.5[21]	4.56	0.06
7-hydroxy-4-methylflavylium	1162.1	4.45[22]	5.21	0.76
BCyP	1211.7	6.5[23]	9.80	3.30
DPI	1225.8	12.8[24]	11.10	-1.70
protonated 6-Aminochrysene	1144.1	3.15[25]	3.54	0.39
6-sulfonate-2-naphthol	1200.8	9.1[26]	8.79	-0.31
naphthalen-1-aminium	1146.6	3.9[27]	3.77	-0.13
naphthalen-2-aminium	1143.6	4.1[27]	3.49	-0.61
CBCyP	1197.8	6.0[28]	8.51	2.51
3HF	1204.0	9.6[29]	9.09	-0.51
Protonated DEA3HF	1166.6	3.25[29]	5.62	2.37
DEA3HF	1211.2	10.54[29]	9.75	-0.79
F3HF	1201.8	10.33[29]	8.88	-1.45
Protonated 1H-phenanthro [9,10-d] imidazole	1156.5	4.65[30]	4.68	0.03
1H-phenanthro[9,10-d] imidazole	1220.7	11.86[30]	10.64	-1.22

Photoacids	ΔG (kJ/mol)	pK_a (Expt.)	pK_a (Calc.)	Error
OG488 (N-A)	1160.6	3.61[31]	5.07	1.46
OG488 (C-N)	1131.4	1.02[31]	2.36	1.34
EG-dHONI	1197.6	8.8[32]	8.49	-0.31
COOH-dHONI	1193.0	8.8[32]	8.07	-0.73
EG-SHONI	1192.0	8.0[32]	7.97	-0.03
HCD	1179.0	5.4[33]	6.77	1.37
o-cyanophenol	1175.3	6.97[34]	6.43	-0.54
m-cyanophenol	1198.2	8.4[34]	8.55	0.21
p-cyanophenol	1189.0	7.74[34]	7.70	-0.04
3,4-dicyanophenol	1175.0	6.5[35]	6.40	-0.10
phenol	1211.9	10.0[36]	9.82	-0.18
m-fluorophenol	1202.1	9.21[36]	8.91	-0.30
p-fluorophenol	1210.6	9.91[36]	9.70	-0.21
m-chlorophenol	1201.4	9.13[36]	8.85	-0.28
p-chlorophenol	1205.4	9.42[36]	9.22	-0.20
m-bromophenol	1202.8	9.03[36]	8.97	-0.06
p-bromophenol	1205.9	9.36[36]	9.26	-0.10
m-methylphenol	1212.7	10.09[36]	9.89	-0.20
p-methylphenol	1220.1	10.26[36]	10.58	0.32
m-ethylphenol	1220.2	10.07[36]	10.59	0.52
p-ethylphenol	1221.4	10.21[36]	10.70	0.49
p-sulfonate-phenol	1198.3	9.03[36]	8.56	-0.47
p-trimethylaminophenol	1199.5	8.35[36]	8.67	0.32
5-bromo-8-hydroxyquinoline	1161.4		5.14	
5-sulfonate-8-hydroxyquinoline	1153.5		4.41	
5-thiocyano-8-hydroxyquinoline	1141.7		3.31	
7-fluoro-8-hydroxyquinoline	1158.2		4.85	
7-chloro-8-hydroxyquinoline	1150.1		4.09	
7-bromo-8-hydroxyquinoline	1149.9		4.07	
7-sulfonate-8-hydroxyquinoline	1169.9		5.93	
7-chloro-5-fluoro-8-hydroxyquinoline	1147.6		3.86	
5,7-dichloro-8-hydroxyquinoline	1140.0		3.16	
5-bromo-7-chloro-8-hydroxyquinoline	1139.1		3.07	
7-bromo-5-fluoro-8-hydroxyquinoline	1146.0		3.71	
7-bromo-5-chloro-8-hydroxyquinoline	1137.7		2.95	
5,7-dibromo-8-hydroxyquinoline	1136.0		2.79	
5,7-disulfonate-8-hydroxyquinoline	1152.0		4.27	

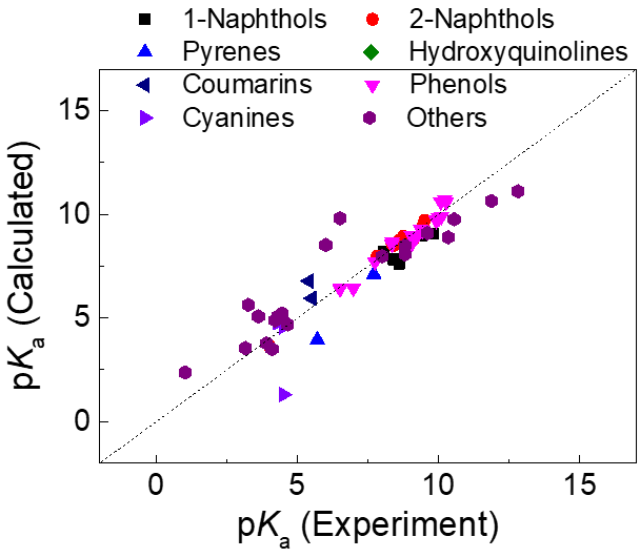


Figure S1. Experimental and calculated pK_a values. Calculated pK_a values were obtained using DFT-calculated ΔG in Eq. (4). The mean absolute error is 0.62 pK_a units.

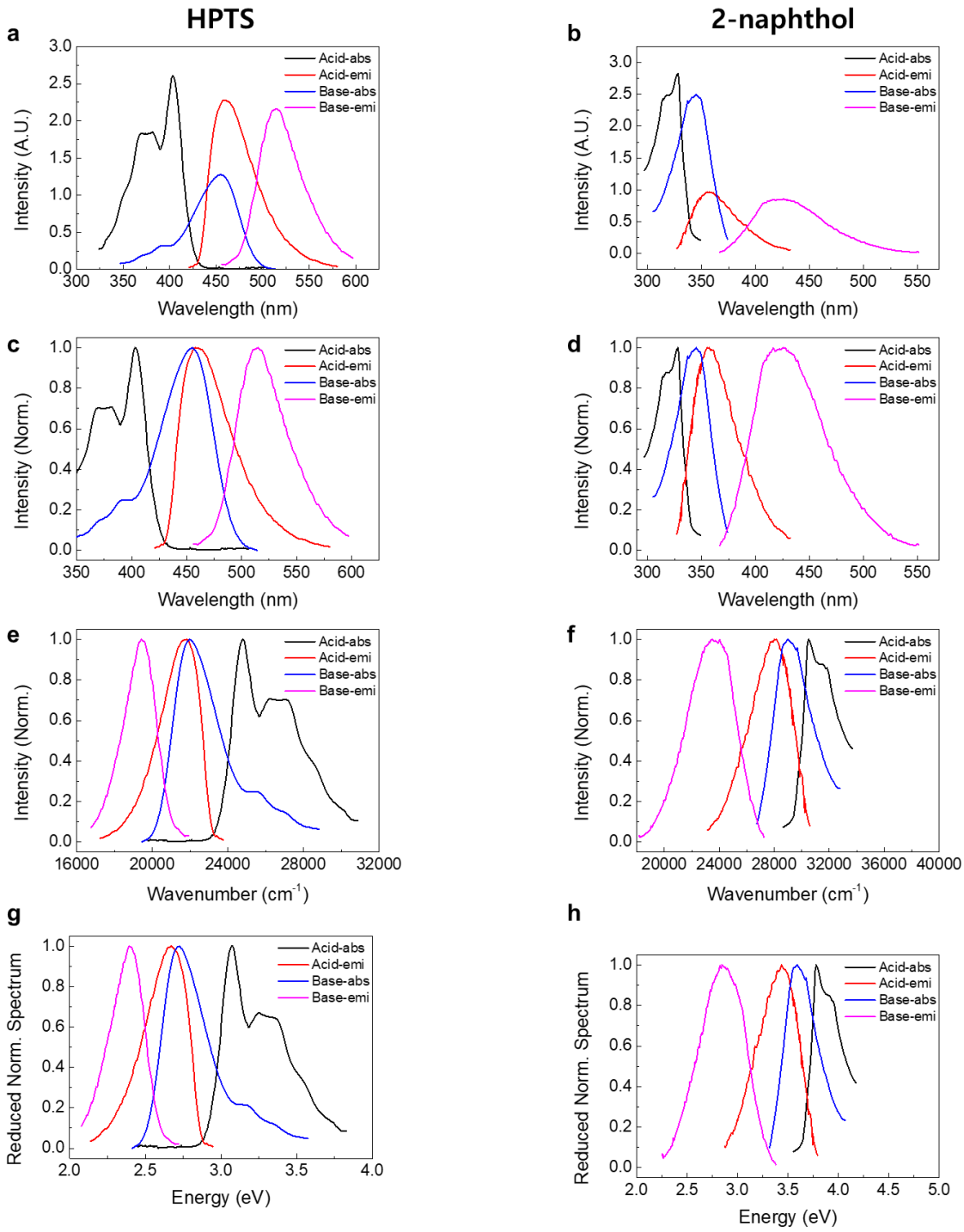


Figure S2. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g** and **h**) the reduced normalized spectra of HPTS and 2-naphthol.

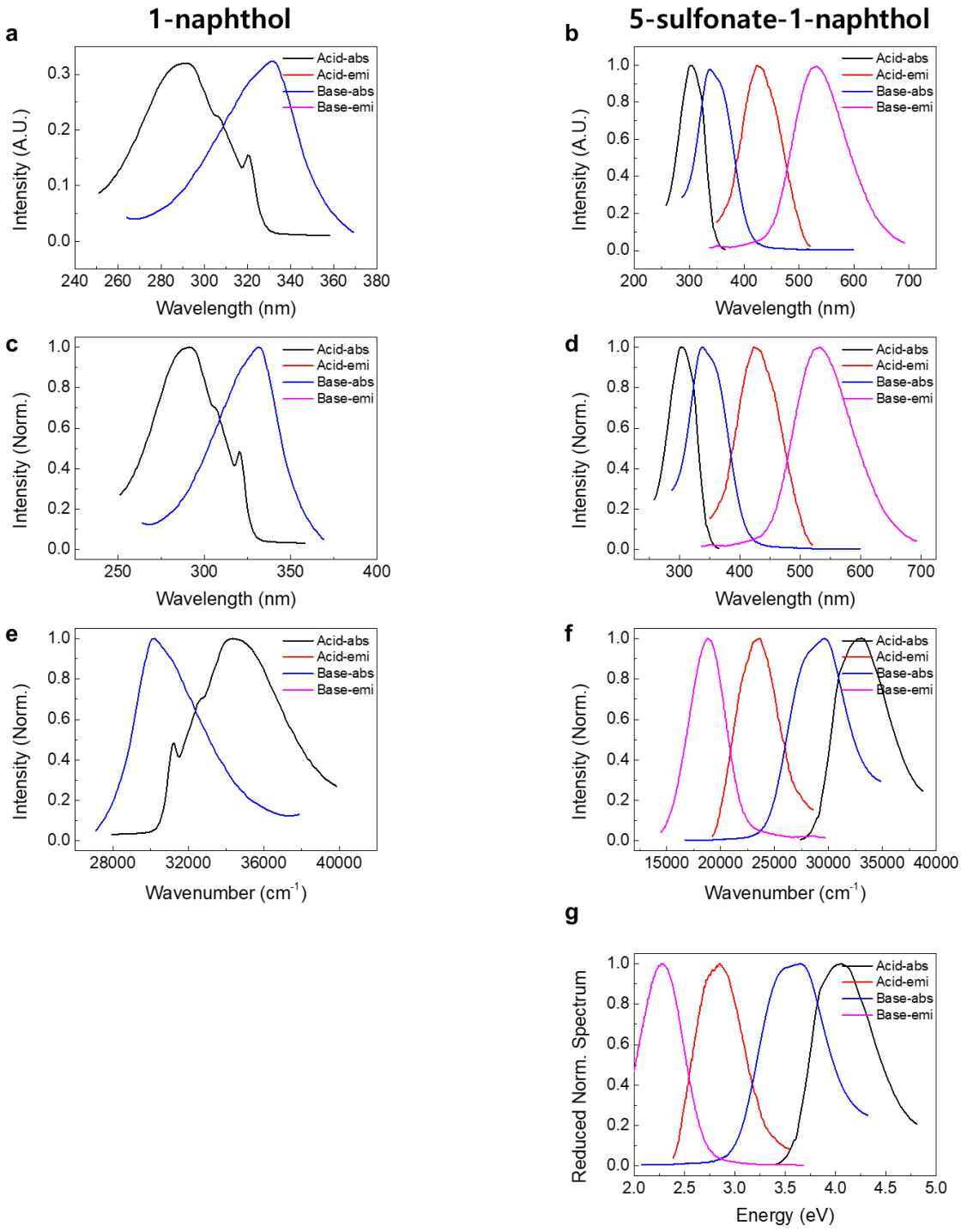


Figure S3. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g**) the reduced normalized spectra of 1-naphtnol and 5-sulfonate-1-naphthol.

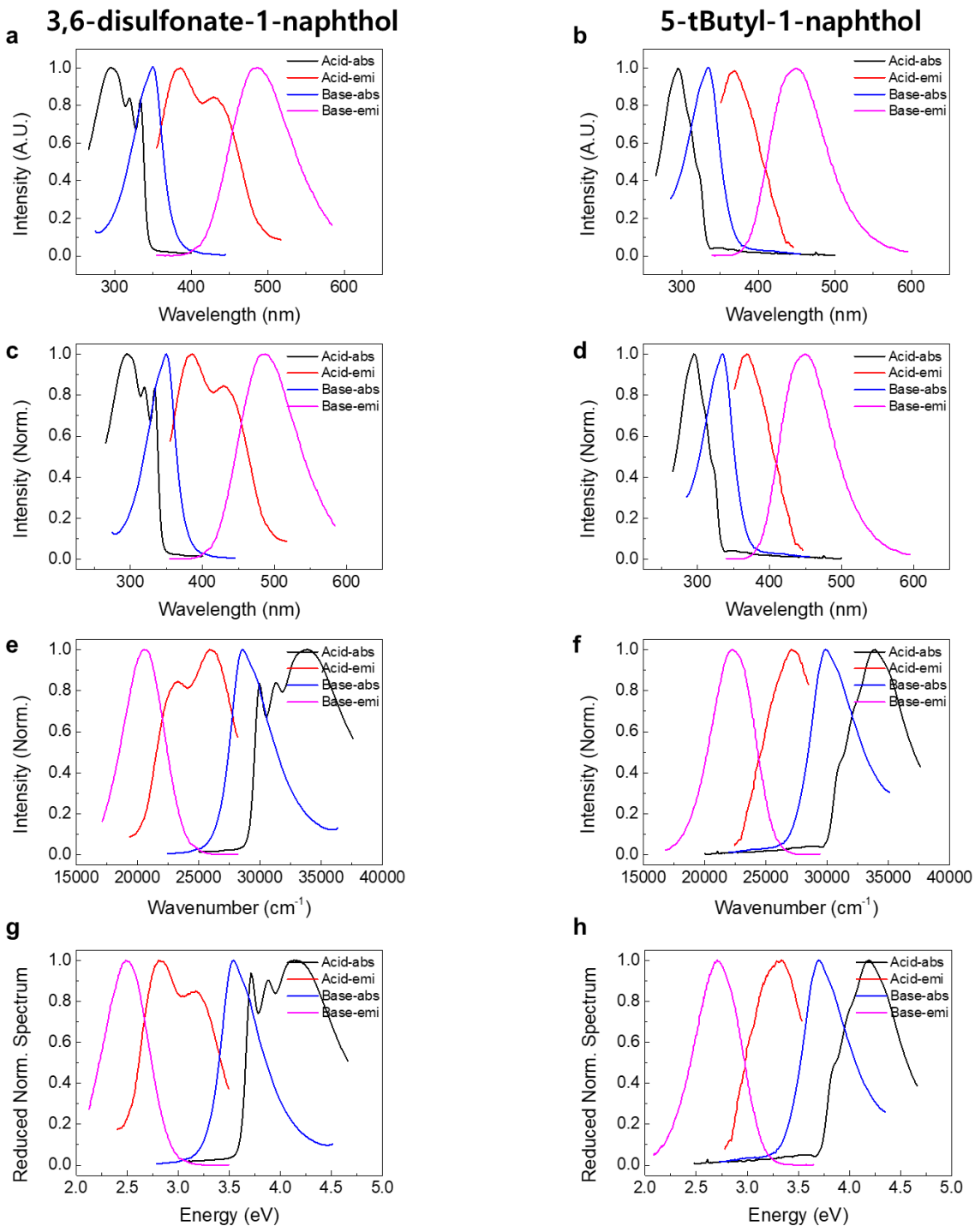


Figure S4. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g** and **h**) the reduced normalized spectra of 3,6-disulfonate-1-naphthol and 5-tButyl-1-naphthol.

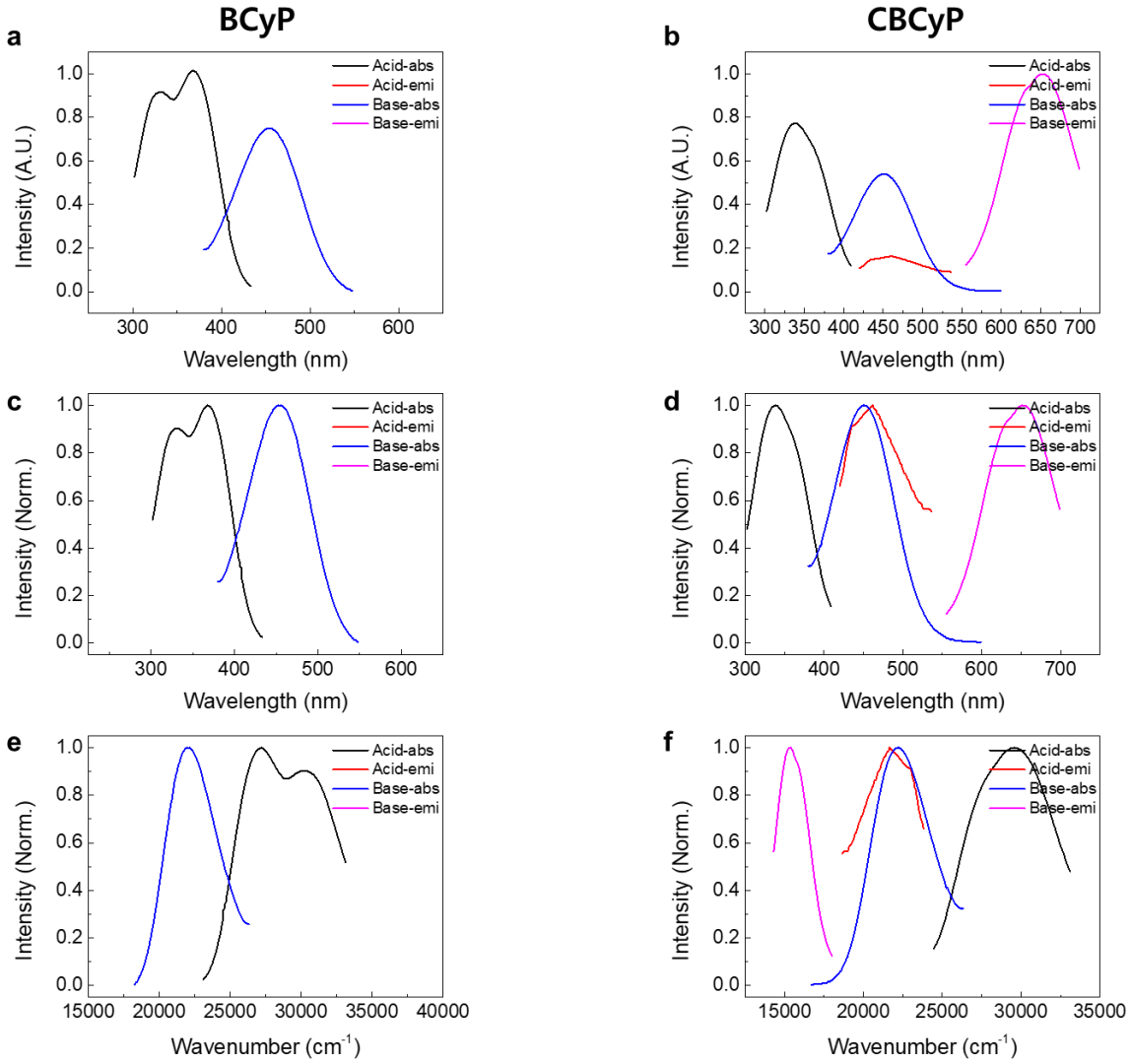


Figure S5. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, and (**e** and **f**) the normalized spectra in wavenumber of BCyP and CBCyP.

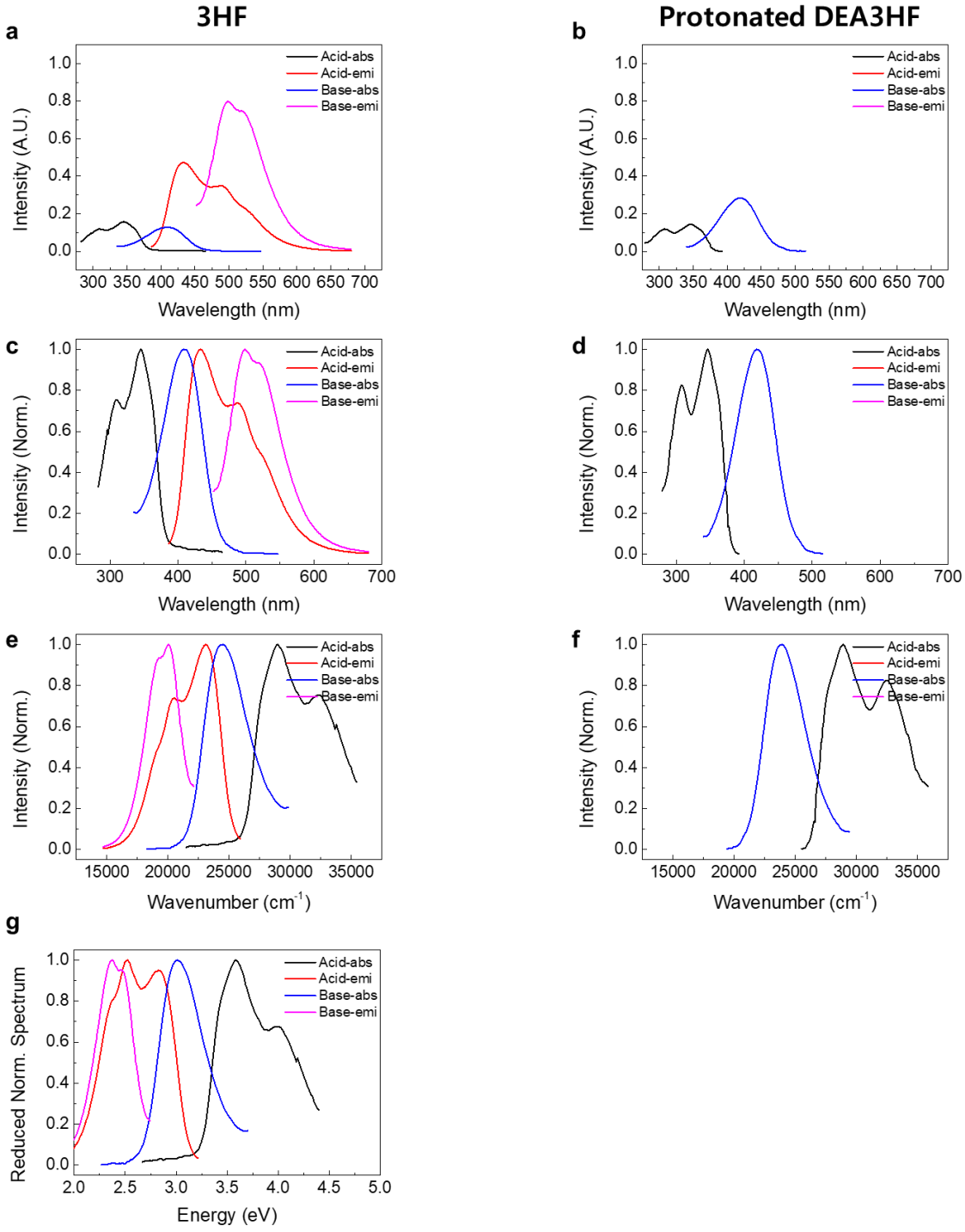


Figure S6. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g**) the reduced normalized spectra of 3HF and Protonated DEA3HF.

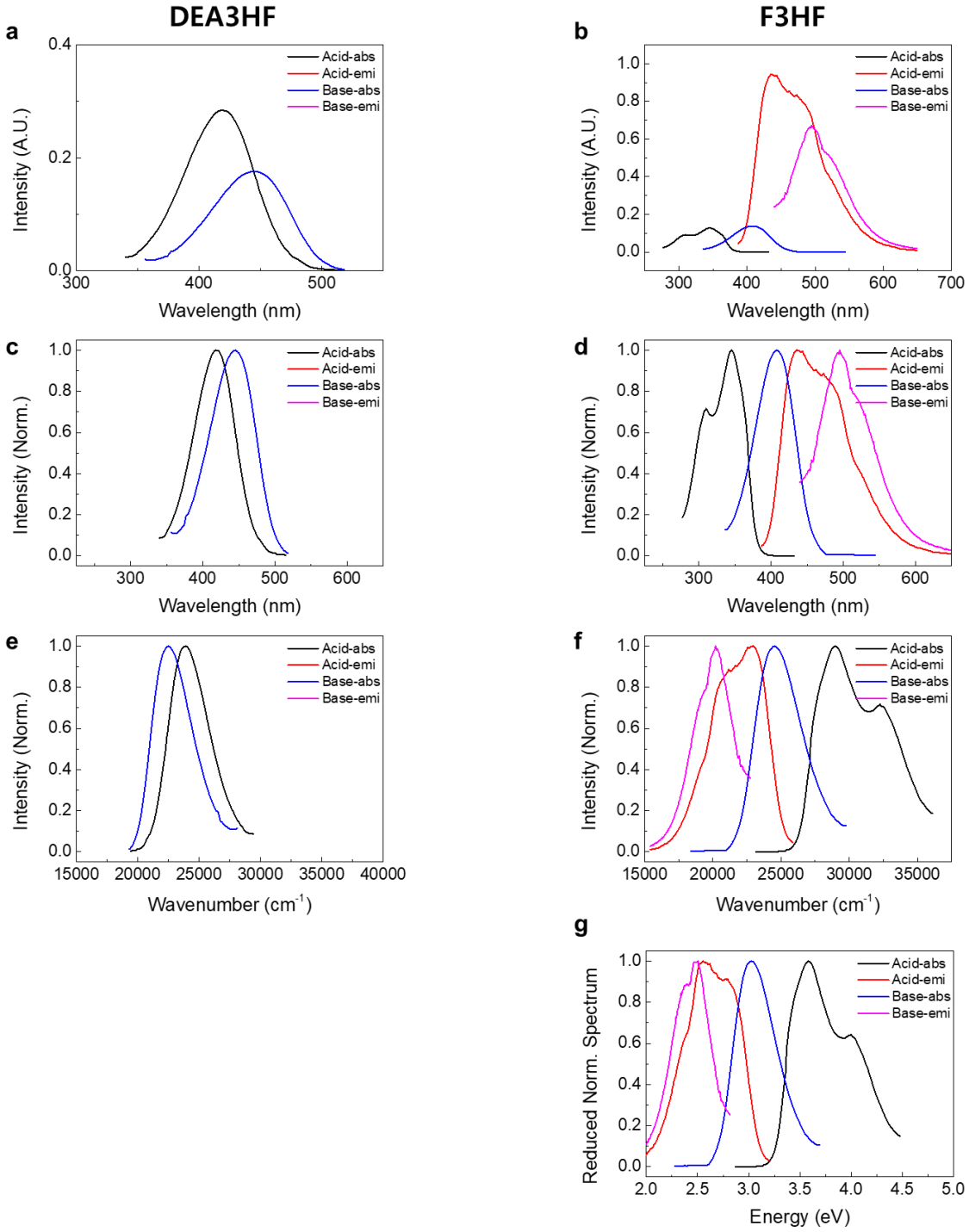


Figure S7. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g**) the reduced normalized spectra of DEA3HF and F3HF.

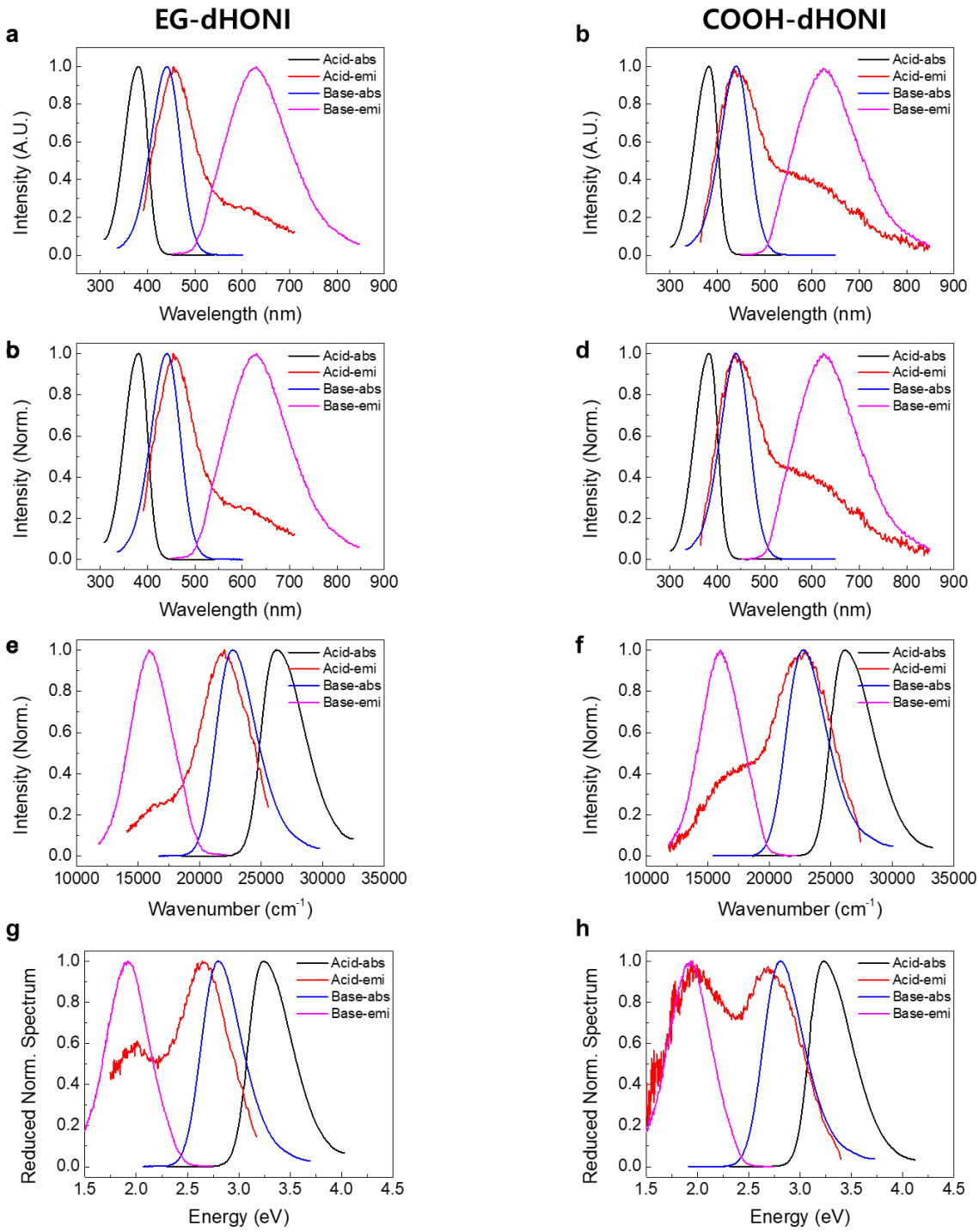


Figure S8. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g** and **h**) the reduced normalized spectra of EG-dHONI and COOH-dHONI.

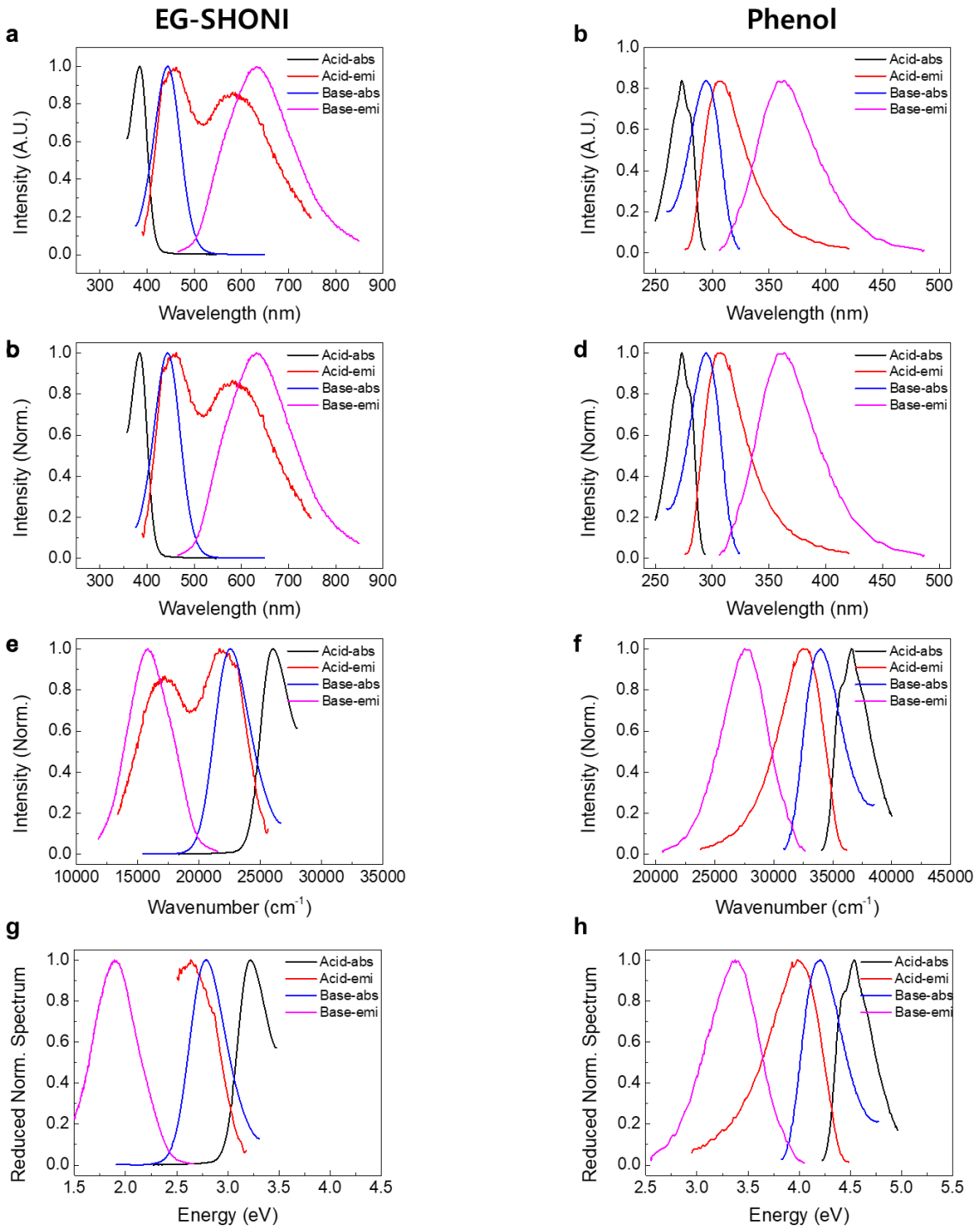


Figure S9. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g** and **h**) the reduced normalized spectra of EG-SHONI and phenol.

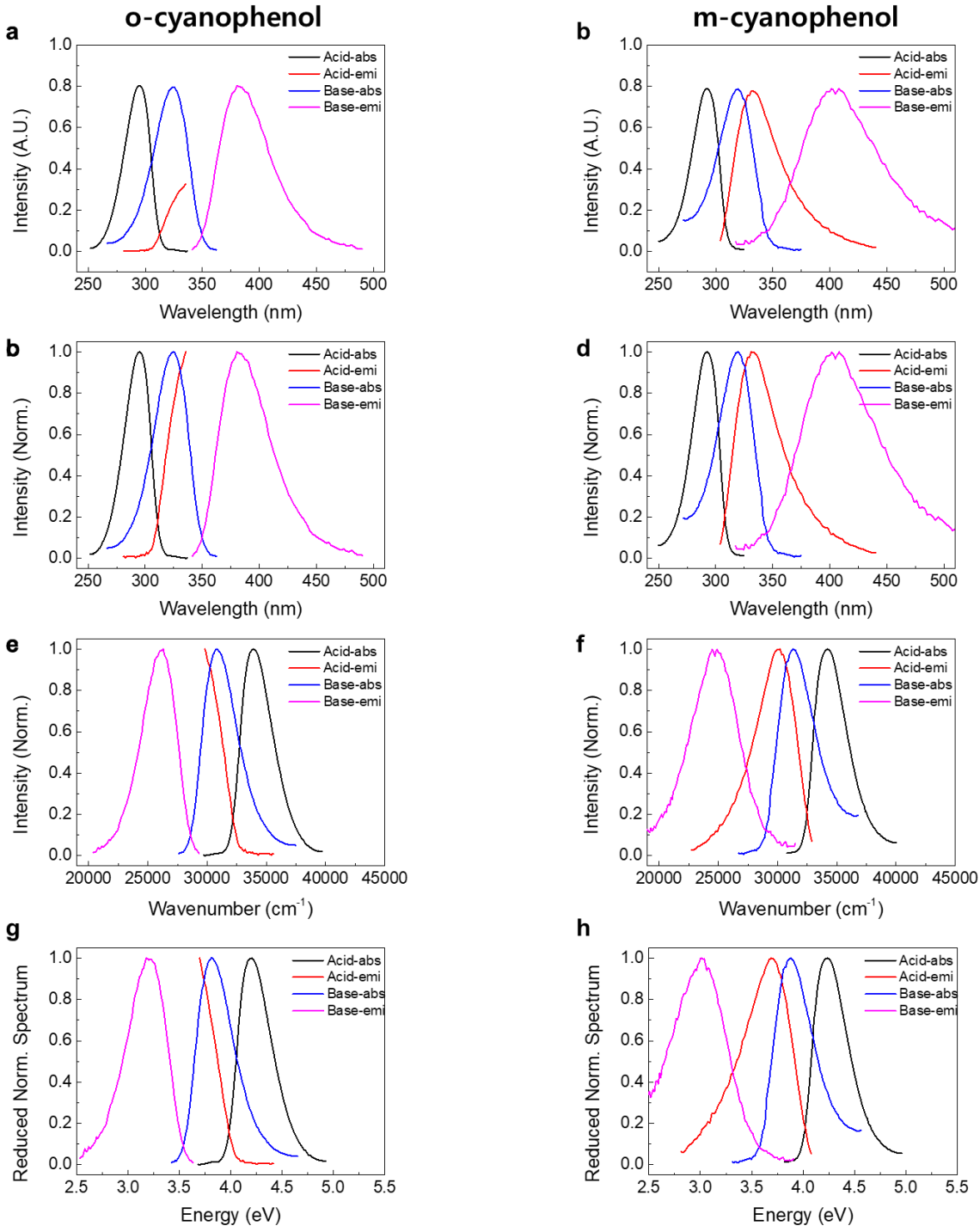


Figure S10. The absorption and emission spectra of acidic and basic forms of photoacids. (**a** and **b**) Raw spectra, (**c** and **d**) the normalized spectra in wavelength, (**e** and **f**) the normalized spectra in wavenumber, and (**g** and **h**) the reduced normalized spectra of o-cyanophenol and m-cyanophenol.

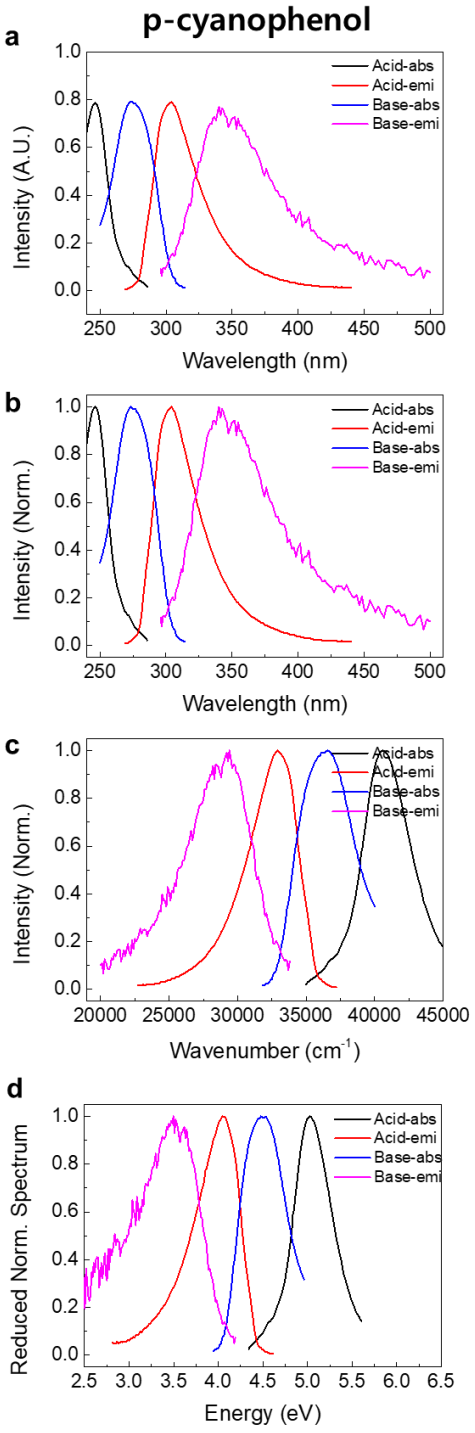


Figure S11. The absorption and emission spectra of acidic and basic forms of p-cyanophenol. (**a**) Raw spectra, (**b**) the normalized spectra in wavelength, (**c**) the normalized spectra in wavenumber, and (**d**) the reduced normalized spectra of p-cyanophenol.

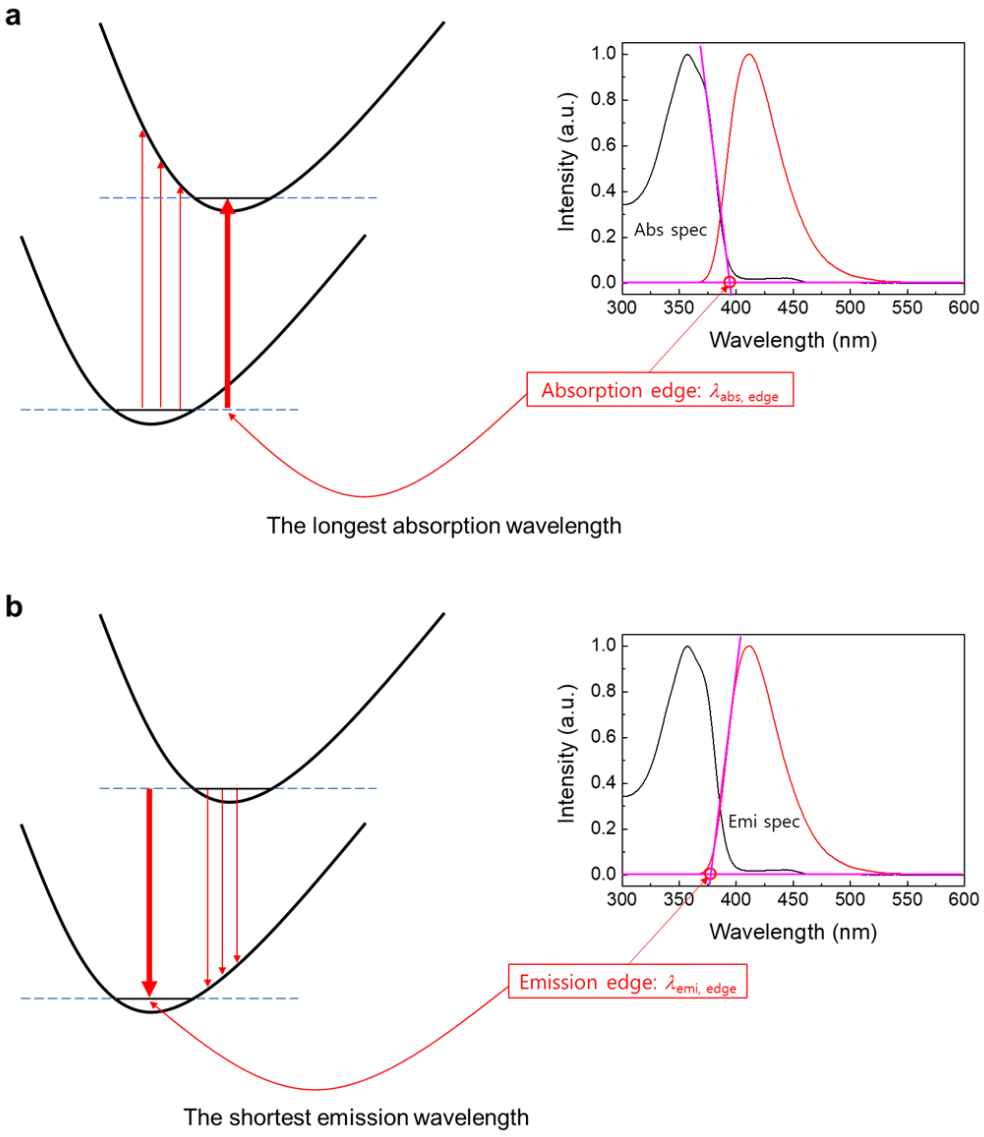


Figure S12. Schematic of obtaining (a) the absorption edge and (b) the emission edge from absorption and emission spectra.

Table S5. The wavelengths (nm) corresponding to the maximum (Max), absorption edge (Abs. edge), emission edge (Emi. edge), the first moment (Mom.), and crossing point (Cross).

Photoacids	Acidic form							Basic form						
	Abs. Max.	Abs. edge	Abs. Mom.	Emi. Max.	Emi. edge	Emi. Mom.	Cross	Abs. Max.	Abs. edge	Abs. Mom.	Emi. Max.	Emi. edge	Emi. Mom.	Cross
Coumarin 183	357.0	393.2	366.6	410.8	378.7	424.4	387.0	443.0	462.7	401.2	451.0	424.6	466.8	447.8
HPTS	403.0	426.9	383.8	458.0	429.5	476.6	430.0	455.0	495.6	439.5	515.0	474.7	523.6	485.0
2-naphthol	328.0	340.7	318.9	355.0	326.5	367.7	336.0	345.0	374.2	339.7	426.0	371.8	437.5	376.0
1-naphthol	291.0	329.1	290.5					331.0	362.7	320.8				
5-sulfonate-1-naphthol	303.0	347.2	303.0	424.0	362.1	430.2	349.0	338.0	412.8	349.0	533.0	446.4	542.1	435.0
3,6-disulfonate-1-naphthol	295.0	344.6	304.3	386.0	329.4	415.6	342.0	350.0	381.2	338.8	487.0	416.6	495.6	407.0
5-tButyl-1-naphthol	295.0	334.3	302.4	369.0	301.4	383.4	327.0	335.0	370.9	330.3	449.0	387.8	460.3	387.0
BCyP	368.0	423.8	355.3					452.0	528.7	451.8				
CBCyP	338.0	415.5	348.1	462.0	387.4	473.7		451.0	530.9	451.5	651.0	560.3	640.2	
3HF	345.0	382.8	334.2	433.0	394.3	475.5	391.0	408.0	462.5	403.4	498.0	449.5	521.4	453.0
Protonated DEA3HF	346.0	380.5	330.2					418.0	474.3	414.7				
DEA3HF	418.0	474.3	414.7					445.0	501.8	437.6				
F3HF	345.0	380.4	331.9	435.0	395.7	472.7	387.0	408.0	459.8	403.2	495.0	431.7	510.3	447.0
EG-dHONI	382.0	421.8	372.0	454.0	374.8	503.7	408.0	441.0	501.2	434.5	630.0	502.1	643.6	509.0
COOH-dHONI	382.0	419.7	372.5	436.0	360.2	525.0	405.0	439.0	501.2	433.1	624.0	505.0	643.4	511.0
EG-SHONI	384.0	418.8	384.6	461.0	391.9	552.4	410.0	444.0	504.5	441.6	632.0	499.1	647.6	511.0
o-cyanophenol	295.0	313.4	291.0	335.6	306.2		311.5	324.7	352.3	319.1	380.2	348.7	394.5	350.9
m-cyanophenol	292.4	311.6	288.0	331.1	303.2	347.3	308.6	319.5	347.7	313.9	404.9	345.5	423.7	347.2
p-cyanophenol	246.3	266.0	246.3	304.0	279.3	319.4	280.1	273.2	306.2	275.8	340.1	297.9	372.0	303.0
phenol	273.2	292.1	271.3	307.7	280.6	321.9	286.9	294.6	321.6	291.0	363.6	315.2	372.8	318.0

Table S6. Calculated ΔG^* and the pK_a^* values by the Förster cycle with the $E_{0\text{-}0}$ values defined by the maximum absorption wavelength (Abs. Max.), maximum emission wavelength (Emi. Max.), average of maximum absorption and emission wavelengths (Avg. Max.), average of the first moments of absorption and emission spectra (1st Mom.), crossing point (Cross), and optical bandgap (OB).

Photoacids	ΔG^* (kJ/mol)	Abs. Max.	Emi. Max.	Avg. Max.	1st Mom.	Cross	OB
Coumarin 183	1139.2	–5.90	0.95	–2.47	0.79	–1.85	–1.50
HPTS	1146.1	1.76	2.63	2.19	2.27	2.17	1.97
2-naphthol	1173.3	6.30	–0.39	2.95	2.89	2.81	2.78
1-naphthol	1140.0	0.69			2.60		3.49
5-sulfonate-1-naphthol	1123.7	1.24	–1.71	–0.24	–1.19	–3.47	–1.86
3,6-disulfonate-1-naphthol	1138.0	–2.57	–2.66	–2.61	1.02	–1.19	–0.98
5-tButyl-1-naphthol	1144.0	1.32	–0.32	0.50	2.30	–0.14	–1.04
BCyP	1151.4	–4.09			–6.10		–3.32
CBCyP	1127.8	-9.54	–7.17	–8.36	–6.65		–7.83
3HF	1147.7	0.22	3.28	1.75	2.28	2.26	1.61
Protonated DEA3HF	1107.7	–7.19			–9.69		–7.65
DEA3HF	1213.9	7.50			7.90		8.12
F3HF	1159.7	0.95	4.49	2.72	3.11	3.06	3.36
EG-dHONI	1143.5	1.46	–4.10	–1.32	0.23	–1.40	–2.23
COOH-dHONI	1114.7	1.67	–5.69	–2.01	1.19	–1.94	–3.61
EG-SHONI	1038.6	0.62	–4.30	–1.84	1.70	–2.11	–1.99
o-cyanophenol	1138.0	0.47	–0.37	0.05		–0.58	–0.90
m-cyanophenol	1156.9	2.26	–3.19	–0.46	–0.10	0.79	0.62
p-cyanophenol	1152.8	–0.65	0.40	–0.12	–1.45	2.08	0.21
phenol	1205.6	4.44	–0.48	1.98	2.95	2.87	2.61

Table S7. pK_a^* values of photoacids obtained from differently-defined $E_{0\text{-}0}$ values.

Photoacids	Abs. Max.	Emi. Max.	Avg. Max.	Crossing point	Optical bandgap
C183	–5.90	0.95	–2.47	–1.85	–1.50
HPTS	1.76	2.63	2.19	2.17	1.97
2naphthol	6.30	–0.39	2.95	2.81	2.78
1naphthol	0.69				3.49
1naphthol-5sulfonate	1.24	–1.71	–0.24	–3.47	–1.86
1naphthol-3,6-disulfonate	–2.57	–2.66	–2.61	–1.19	–0.98
1naphthol-5tBu	1.32	–0.32	0.50	–0.14	–1.04
BCyP	–4.09				–3.32
CBCyP	–9.54	–7.17	–8.36		–7.83
3HF	0.22	3.28	1.75	2.26	1.61
Protonated_DEA3HF	–7.19				–7.65
DEA3HF	7.50				8.12
F3HF	0.95	4.49	2.72	3.06	3.36
EG-dHONI	1.46	–4.10	–1.32	–1.40	–2.23
COOH-dHONI	1.67	–5.69	–2.01	–1.94	–3.61
EG-SHONI	0.62	–4.30	–1.84	–2.11	–1.99
o-cyanophenol	0.47	–0.37	0.05	–0.58	–0.90
m-cyanophenol	2.26	–3.19	–0.46	0.79	0.62
p-cyanophenol	–0.65	0.40	–0.12	2.08	0.21
phenol	4.44	–0.48	1.98	2.87	2.61

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