A water-soluble cyclometalated Iridium(III) complex for pH sensing based on aggregation-induced enhanced phosphorescence

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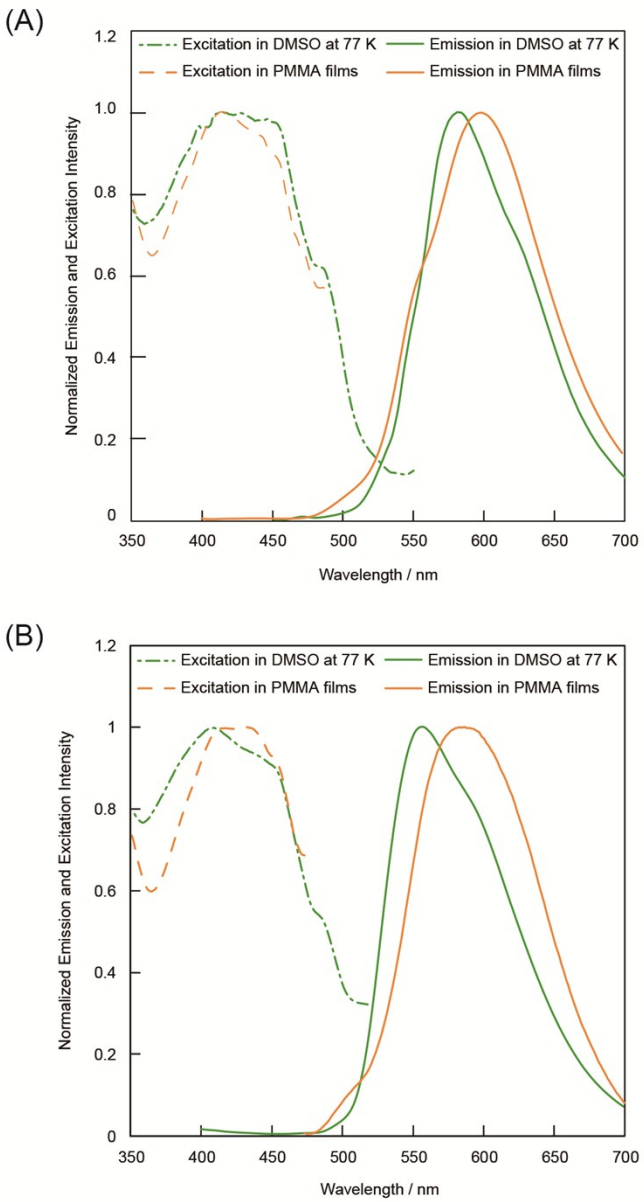

Fig. S1. (A) Emission and excitation spectra of **1** in DMSO at 77K (λ_{ex} = 365 nm, λ_{em} = 582 nm) and PMMA films (λ_{ex} = 365 nm, λ_{em} = 596 nm). (B) Emission and excitation spectra of **2** in DMSO at 77K (λ_{ex} = 365 nm, λ_{em} = 556 nm) and PMMA films (λ_{ex} = 365 nm, λ_{em} = 587 nm).

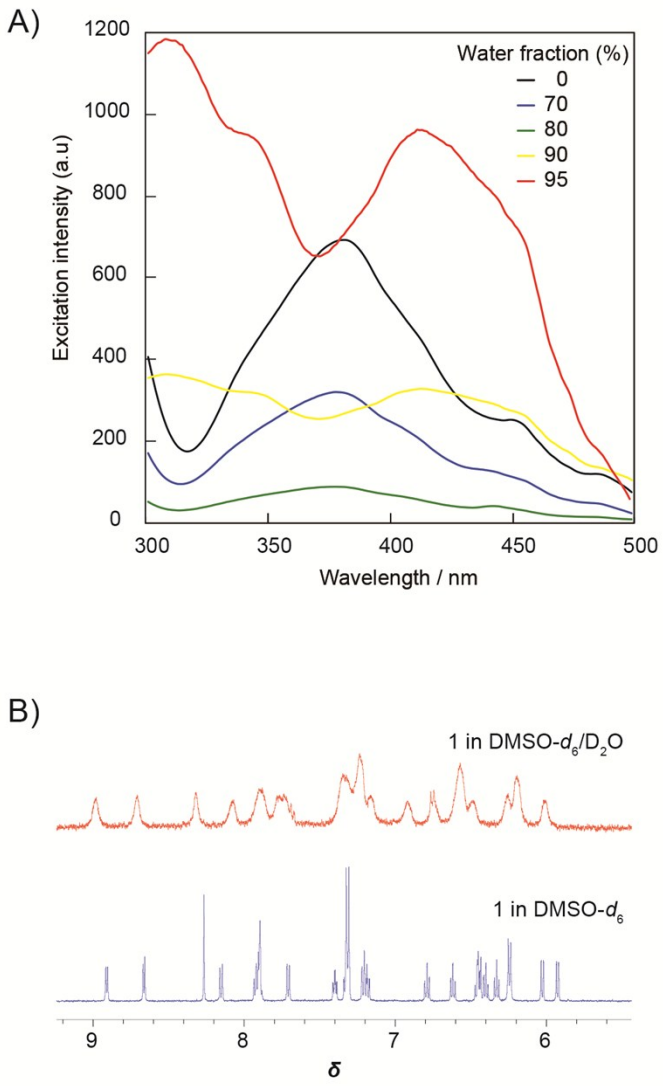

Fig. S2. (A) Excitation spectra of **1** in DMSO/water mixed solutions with different water fractions (0–99% v/v). (B) ^{1}H NMR spectra of **1** in DMSO-d_6/D_2O (top) and DMSO-d_6 alone (bottom).

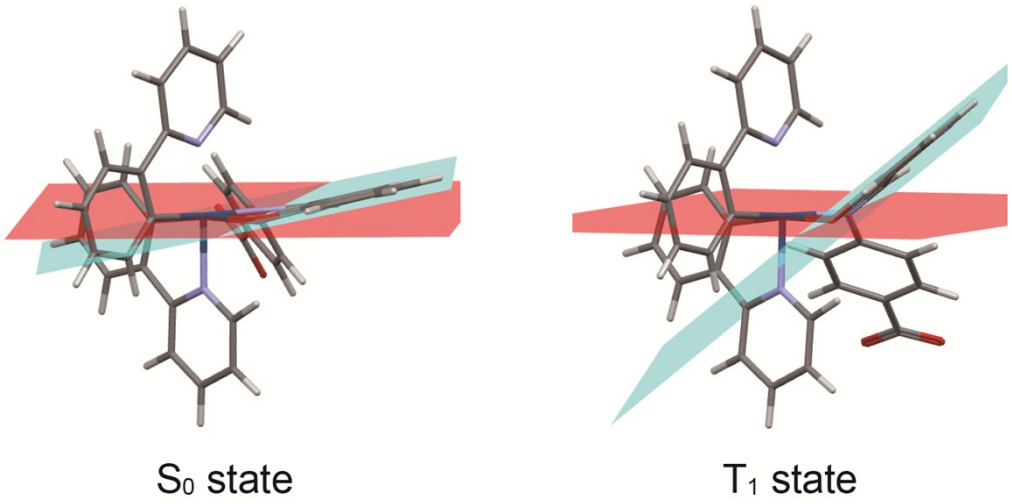

Fig. S3. The optimized structures of **2** at S_0 (left) and T_1 (right) states. Red plane: coordination plane (Ir, N, O); blue plane: $N{=}C_{(SB)}{-}C_{(Ph\text{-}O)}{-}C{-}O$ plane.

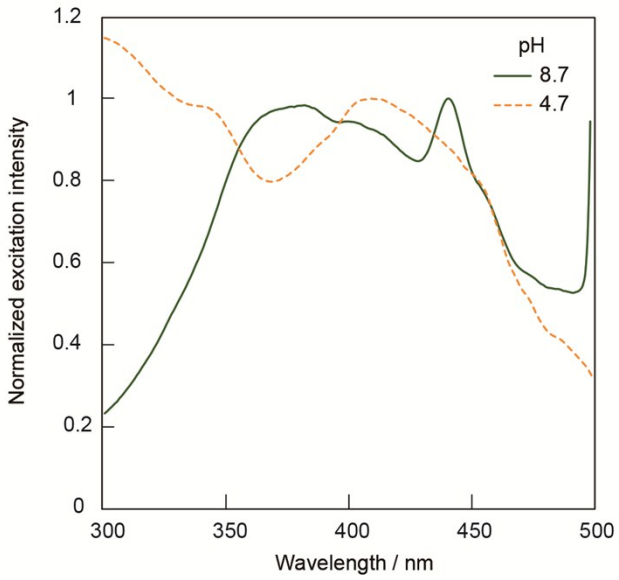

Fig. S4. Emission and excitation spectra of **2** in H_2O at pH 8.7 (λ_{ex} = 365 nm, λ_{em} = 516 nm) and 4.7 (λ_{ex} = 365 nm, λ_{em} = 618 nm).

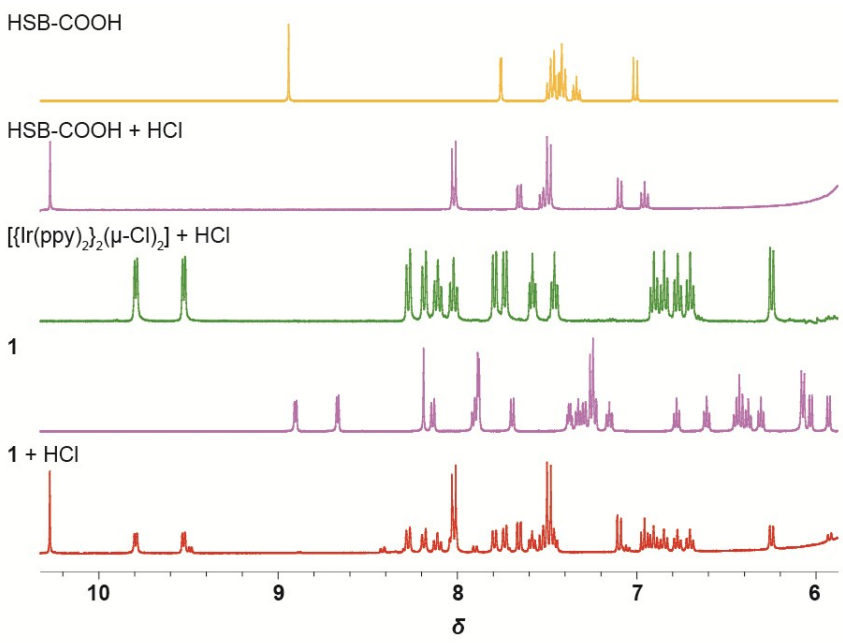

Fig. S5. ^{1}H NMR spectra of HSB-COOH, [{Ir(ppy)$_2$}$_2$(μ-Cl)$_2$], and **1** in the absence and presence of HCl in DMSO-d_6.

Table S1. Cartesian coordinates of the optimized **1** in the ground state (S_0) using the PCM method for DMSO.

C	-0.163923	0.269026	3.078557	C	-2.440134	-2.364833	1.549531
H	-0.955278	0.995401	2.935287	H	-1.786155	-2.285982	2.413494
C	0.474285	0.083307	4.296671	C	-2.192498	-1.577153	0.412795
H	0.188076	0.683517	5.152568	C	-2.092510	2.612990	0.691871
C	1.478458	-0.885726	4.382267	C	-3.260036	3.381233	0.997190
H	1.999918	-1.058333	5.318360	H	-4.132374	2.833354	1.341741
C	1.804106	-1.630662	3.255355	C	-3.292477	4.753763	0.859490
H	2.579316	-2.385772	3.307175	H	-4.206704	5.292295	1.097224
C	1.129577	-1.408066	2.046381	C	-2.155842	5.467199	0.418704
C	1.347722	-2.117558	0.783362	H	-2.184862	6.546989	0.317535
C	2.287240	-3.151699	0.631555	C	-1.007489	4.761315	0.128905
H	2.908791	-3.461365	1.467187	H	-0.117291	5.292398	-0.201190
C	2.427627	-3.794191	-0.594882	C	-0.934950	3.344356	0.240225
H	3.152547	-4.594153	-0.712136	C	0.340595	2.764302	-0.066990
C	1.619816	-3.404028	-1.670475	H	1.133484	3.499222	-0.234087
H	1.719429	-3.907352	-2.629358	C	2.066037	1.263143	-0.403654
C	0.687915	-2.374303	-1.522702	C	2.502516	0.555694	-1.534214
H	0.079520	-2.091924	-2.377815	H	1.774770	0.190997	-2.248066
C	0.530615	-1.691941	-0.303219	C	3.858453	0.329658	-1.738610
C	-1.325220	0.737890	-2.708329	H	4.188446	-0.207477	-2.620290
H	-0.458592	1.357764	-2.518468	C	4.804401	0.795493	-0.810588
C	-2.007226	0.792773	-3.915667	C	4.367458	1.494576	0.322375
H	-1.668487	1.466139	-4.694404	H	5.101193	1.847395	1.038965
C	-3.122147	-0.030780	-4.089063	C	3.011482	1.727994	0.525683
H	-3.681360	-0.016972	-5.019050	H	2.673812	2.256109	1.411539
C	-3.509702	-0.870372	-3.052608	Ir	-0.745722	-0.198279	0.144127
H	-4.372948	-1.514451	-3.168579	N	0.154050	-0.452447	1.986663
C	-2.786333	-0.890114	-1.851874	N	-1.693907	-0.079913	-1.702560
C	-3.081919	-1.727157	-0.686122	N	0.676759	1.506982	-0.199096
C	-4.164450	-2.621982	-0.633011	O	-2.139111	1.330178	0.869913
H	-4.839537	-2.725954	-1.477737	C	6.260969	0.572638	-0.981901
C	-4.384112	-3.385415	0.509777	O	7.119118	0.958639	-0.204894
H	-5.220622	-4.076599	0.551226	O	6.566446	-0.114200	-2.105279
C	-3.517501	-3.253486	1.601109	H	7.534061	-0.206270	-2.125567
H	-3.683338	-3.848116	2.496343				

Table S2. Cartesian coordinates of the optimized **1** in the excited triplet state (T_1) using the PCM method for DMSO.

C	0.849409	-0.559450	2.726160	C	-2.276531	-2.372383	1.606292
H	0.306715	0.352331	2.945370	H	-1.405075	-2.600992	2.212074
C	1.681623	-1.179045	3.647181	C	-2.193032	-1.407824	0.592790
H	1.818329	-0.740429	4.628755	C	-1.701116	2.411707	1.262415
C	2.324732	-2.363533	3.276824	C	-2.797175	3.044087	1.901531
H	2.981607	-2.875047	3.973028	H	-3.386438	2.436907	2.582790
C	2.117351	-2.882603	2.004859	C	-3.110027	4.374382	1.667883
H	2.609589	-3.798977	1.702654	H	-3.960985	4.834204	2.160759
C	1.270037	-2.220333	1.106236	C	-2.311009	5.126604	0.776305
C	0.962422	-2.634985	-0.263773	H	-2.551434	6.168505	0.583438
C	1.512123	-3.776446	-0.867603	C	-1.221439	4.550538	0.148472
H	2.182041	-4.427536	-0.313502	H	-0.606651	5.148054	-0.520351
C	1.205586	-4.083214	-2.190674	C	-0.861687	3.184791	0.352065
H	1.630738	-4.967001	-2.656442	C	0.317303	2.700200	-0.252445
C	0.348668	-3.244814	-2.913499	H	0.921954	3.438150	-0.777886
H	0.108847	-3.480750	-3.947157	C	2.190032	1.297897	-0.328912
C	-0.202531	-2.108943	-2.317035	C	2.802972	0.186357	-0.962348
H	-0.866966	-1.480311	-2.901612	H	2.171770	-0.571327	-1.405102
C	0.089590	-1.768192	-0.985577	C	4.180074	0.085097	-1.059848
C	-1.721500	1.278959	-2.328115	H	4.619947	-0.767363	-1.565738
H	-0.715467	1.674907	-2.348081	C	5.017587	1.081806	-0.521157
C	-2.675229	1.653750	-3.264161	C	4.422696	2.186867	0.117180
H	-2.413233	2.356900	-4.046055	H	5.065837	2.946165	0.549989
C	-3.955914	1.106245	-3.166283	C	3.047663	2.302302	0.205950
H	-4.730146	1.379599	-3.876085	H	2.611101	3.147595	0.726316
C	-4.227381	0.194966	-2.153586	Ir	-0.610321	-0.220332	0.103080
H	-5.210886	-0.251235	-2.072709	N	0.650323	-1.065129	1.493710
C	-3.226716	-0.161400	-1.239238	N	-1.987666	0.407681	-1.335710
C	-3.364401	-1.151855	-0.166654	N	0.809278	1.404521	-0.257021
C	-4.563950	-1.832705	0.098475	O	-1.431676	1.164434	1.547681
H	-5.457940	-1.629040	-0.483484	C	6.486803	1.014208	-0.595153
C	-4.618600	-2.780032	1.116779	O	7.254365	1.856294	-0.150007
H	-5.546645	-3.305101	1.321902	O	6.945033	-0.101715	-1.219417
C	-3.470796	-3.049038	1.869210	H	7.914551	-0.039107	-1.211065
H	-3.507593	-3.788943	2.664828				

Table S3. Cartesian coordinates of the optimized **2** in the ground state (S_0) using the PCM method for DMSO.

C	-0.138523	0.240481	3.081473	H	-3.712109	-3.837862	2.462999
H	-0.924226	0.974600	2.946204	C	-2.452324	-2.359116	1.530681
C	0.503076	0.040339	4.295524	H	-1.796158	-2.297912	2.394618
H	0.225372	0.636430	5.157136	C	-2.195440	-1.561141	0.402664
C	1.500069	-0.937175	4.369529	C	-2.043605	2.622900	0.724995
H	2.024479	-1.120731	5.301926	C	-3.197431	3.404624	1.044605
C	1.814785	-1.676048	3.235681	H	-4.073955	2.866675	1.394618
H	2.584641	-2.437201	3.278114	C	-3.213726	4.779220	0.914060
C	1.136856	-1.439078	2.031141	H	-4.118763	5.328321	1.163001
C	1.342646	-2.141822	0.762695	C	-2.072526	5.478086	0.466356
C	2.268697	-3.186784	0.601274	H	-2.086540	6.558706	0.369747
H	2.889172	-3.509419	1.432849	C	-0.935683	4.756038	0.163274
C	2.397379	-3.822772	-0.629685	H	-0.041011	5.276596	-0.171887
H	3.112200	-4.630614	-0.754866	C	-0.881015	3.339737	0.268015
C	1.591145	-3.414890	-1.700070	C	0.388067	2.741951	-0.053323
H	1.682210	-3.912451	-2.662902	H	1.189454	3.467754	-0.220660
C	0.672711	-2.374864	-1.542566	C	2.102861	1.231675	-0.412943
H	0.066148	-2.078447	-2.394307	C	2.530054	0.554171	-1.563438
C	0.527118	-1.698763	-0.318038	H	1.794933	0.208090	-2.281224
C	-1.299866	0.769700	-2.698289	C	3.889034	0.335422	-1.778028
H	-0.422707	1.373242	-2.504426	H	4.233057	-0.177341	-2.670574
C	-1.982645	0.845091	-3.904147	C	4.853206	0.767343	-0.856274
H	-1.634362	1.519574	-4.677749	C	4.414563	1.434067	0.292928
C	-3.110444	0.040441	-4.083043	H	5.161110	1.762925	1.008699
H	-3.670771	0.071033	-5.012002	C	3.057541	1.669362	0.517319
C	-3.508816	-0.802585	-3.053463	H	2.726507	2.177986	1.418711
H	-4.381556	-1.432970	-3.173741	Ir	-0.731783	-0.196144	0.145141
C	-2.784031	-0.843827	-1.854008	N	0.168914	-0.475226	1.982834
C	-3.088991	-1.688771	-0.696236	N	-1.680020	-0.050456	-1.698647
C	-4.182432	-2.570821	-0.651640	N	0.709092	1.484473	-0.190841
H	-4.859735	-2.657524	-1.496659	O	-2.106186	1.337934	0.895637
C	-4.410085	-3.344342	0.482793	C	6.349525	0.514807	-1.099408
H	-5.254862	-4.025843	0.517673	O	7.137570	0.923465	-0.202907
C	-3.540246	-3.235128	1.574251	O	6.648599	-0.076056	-2.173046

Table S4. Cartesian coordinates of the optimized **2** in the excited triplet state (T_1) using the PCM method for DMSO.

C	0.989519	-0.558953	2.630318	H	-3.438980	-3.665820	2.862443
H	0.481601	0.371617	2.855175	C	-2.228079	-2.306103	1.708154
C	1.845762	-1.185698	3.524638	H	-1.331059	-2.550329	2.270303
H	2.039955	-0.734078	4.491001	C	-2.170709	-1.362171	0.671821
C	2.437650	-2.395111	3.147864	C	-1.560276	2.456929	1.275986
H	3.111854	-2.913442	3.822671	C	-2.594808	3.133561	1.967530
C	2.156513	-2.930393	1.896511	H	-3.149468	2.562145	2.707974
H	2.609579	-3.865788	1.589996	C	-2.898305	4.465983	1.720325
C	1.287058	-2.260109	1.025044	H	-3.701467	4.954620	2.265244
C	0.908399	-2.687827	-0.323222	C	-2.162778	5.180973	0.744635
C	1.395387	-3.857585	-0.928710	H	-2.404806	6.220219	0.536834
H	2.064791	-4.522727	-0.389934	C	-1.138167	4.564782	0.056718
C	1.026227	-4.175378	-2.233294	H	-0.568579	5.123533	-0.683268
H	1.403038	-5.080880	-2.700199	C	-0.776712	3.195800	0.287987
C	0.169648	-3.318766	-2.935836	C	0.329258	2.671214	-0.393760
H	-0.118517	-3.561739	-3.956051	H	0.874518	3.353790	-1.044963
C	-0.320119	-2.155746	-2.336650	C	2.214606	1.263793	-0.399110
H	-0.986697	-1.514339	-2.906198	C	2.842861	0.111016	-0.938329
C	0.033297	-1.804060	-1.022288	H	2.219165	-0.680948	-1.331952
C	-1.785878	1.242282	-2.334430	C	4.225626	0.017549	-1.005618
H	-0.770693	1.604539	-2.422638	H	4.696845	-0.861902	-1.433969
C	-2.778302	1.623033	-3.227254	C	5.057674	1.047816	-0.535434
H	-2.538298	2.295384	-4.043155	C	4.441271	2.191138	0.002423
C	-4.068571	1.121194	-3.043241	H	5.081046	2.984655	0.376110
H	-4.873238	1.401427	-3.716030	C	3.061091	2.311933	0.063793
C	-4.309832	0.244419	-1.992762	H	2.611342	3.197233	0.502535
H	-5.300781	-0.168320	-1.846365	Ir	-0.587614	-0.227626	0.074666
C	-3.270053	-0.121171	-1.126426	N	0.718480	-1.080196	1.418166
C	-3.376693	-1.085160	-0.025813	N	-2.021626	0.407698	-1.303163
C	-4.579445	-1.724507	0.319273	N	0.832119	1.361575	-0.350544
H	-5.498627	-1.504945	-0.216679	O	-1.304668	1.205710	1.562783
C	-4.605616	-2.651196	1.358220	C	6.584817	0.932031	-0.605743
H	-5.536576	-3.143597	1.624748	O	7.240028	1.920893	-0.174382
C	-3.425244	-2.941723	2.050958	O	7.042773	-0.141525	-1.085873

Table S5. Structural parameters (selected bond lengths and separations (α, Å) and angle (β, °)) of the optimized structures of **1** and **2**.

complex	**1**		**2**	
state	S_0	T_1	S_0	T_1
$C_{(SB)}$–$C_{(Ph\text{-}O)}$	1.435	1.410	1.439	1.401
$C_{(SB)}$–N	1.308	1.386	1.305	1.404
N–$C_{(Ph\text{-}COO)}$	1.425	1.387	1.434	1.387
Ir–N_1	2.066	2.058	2.065	2.059
Ir–N_2	2.079	2.088	2.078	2.088
Ir1–N	2.247	2.187	2.239	2.173
Ir–O	2.192	2.163	2.192	2.187
Ir–C_1	2.015	2.018	2.014	2.018
Ir–C_2	2.017	2.038	2.018	2.037
α	0.20	0.68	0.22	0.78
β	8.1	29	8.7	34