Supplementary Information

Red fluorophore comprising of a borinate-containing xanthene analogue as a polyol sensor

N. Shimomura,[a] Y. Egawa,*[a] R. Miki,[a] T. Fujihara,[b] Y. Ishimaru[c] and T. Seki[a]

a. Faculty of Pharmaceutical Sciences, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan

b. Research and Development Bureau, Comprehensive Analysis Center for Science, Saitama University, Shimo-ohkubo 255, Sakura-ku, Saitama, Saitama 338-8570, Japan

c. Division of Material Science, Graduate School of Science and Engineering, Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama, Saitama, 338-8570, Japan

Contents

NMR spectra

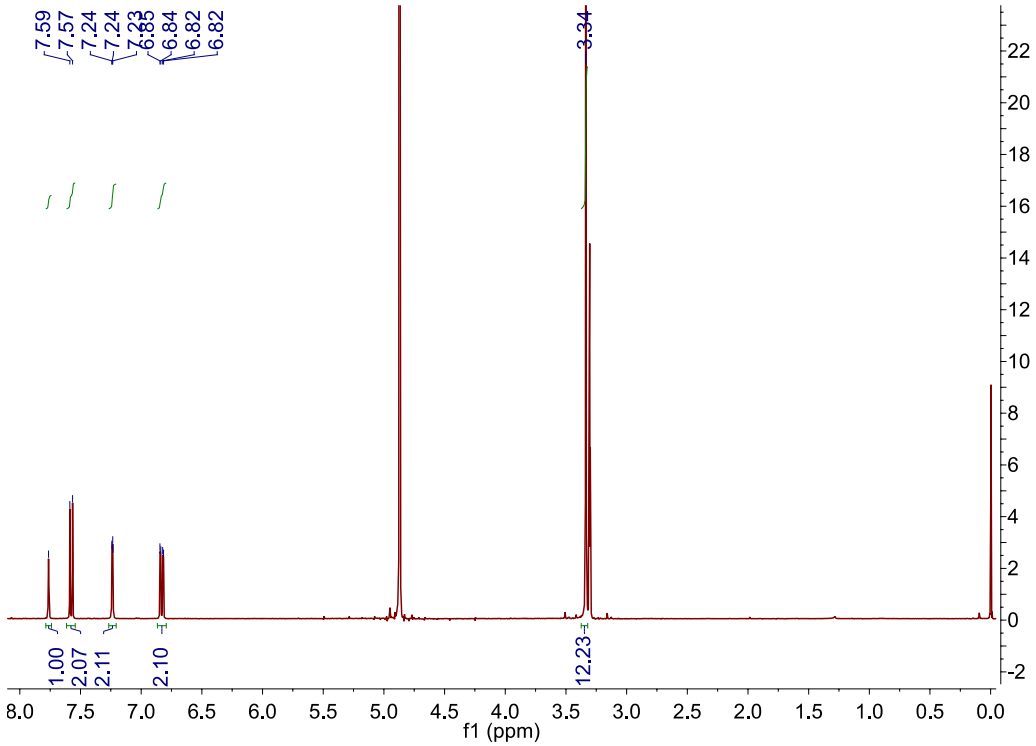

Fig. S1 ^{1}H NMR spectrum of JS-R (borinic acid form) in CD_3OD.

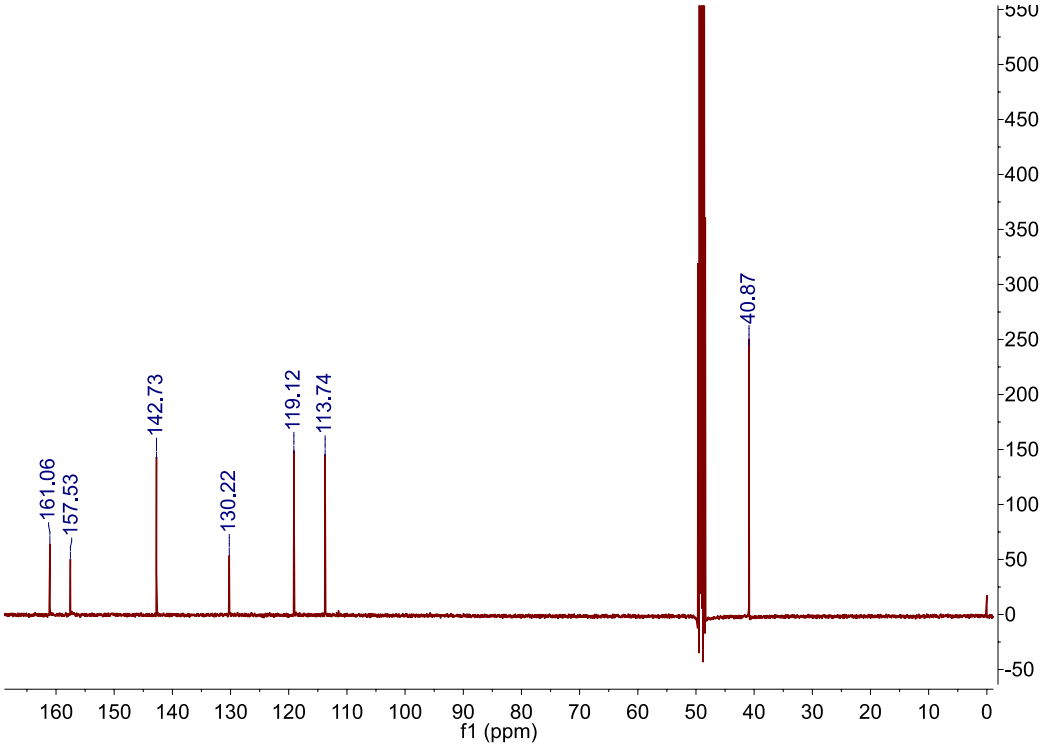

Fig. S2 ^{13}C NMR spectrum of JS-R (borinic acid form) in CD_3OD. A signal due to the carbon atom directly attached to the boron atom could not be detected.

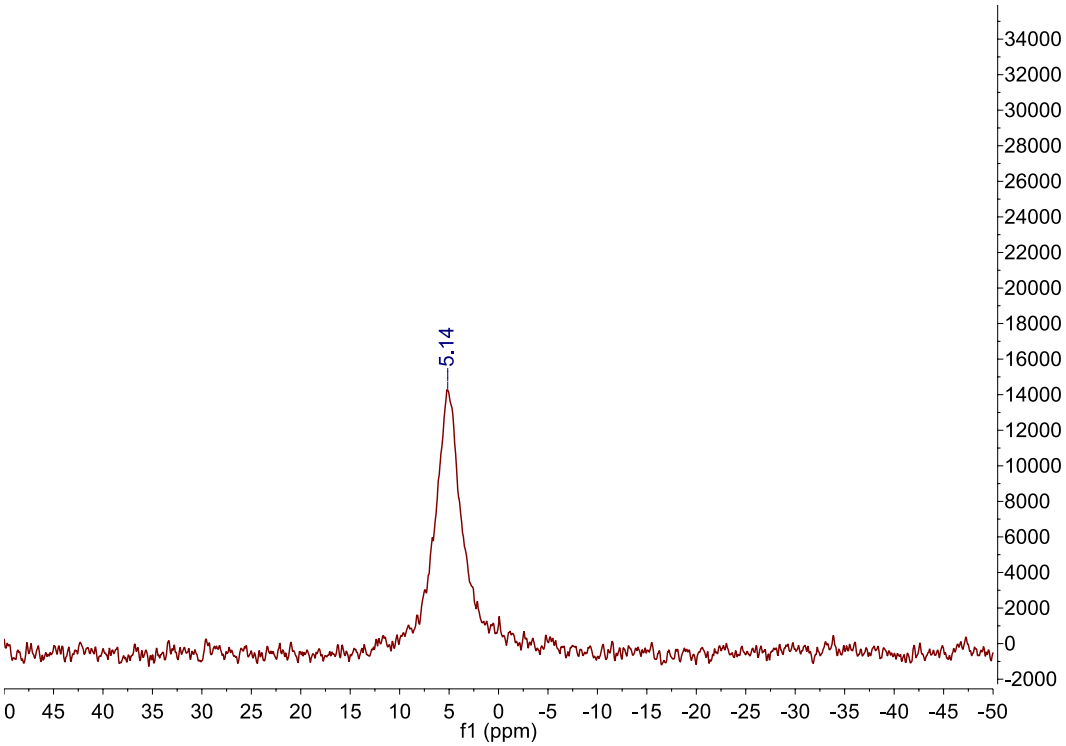

Fig. S3 ^{11}B NMR spectrum of JS-R (borinic acid form) in CD_3OD.

Crystal structures

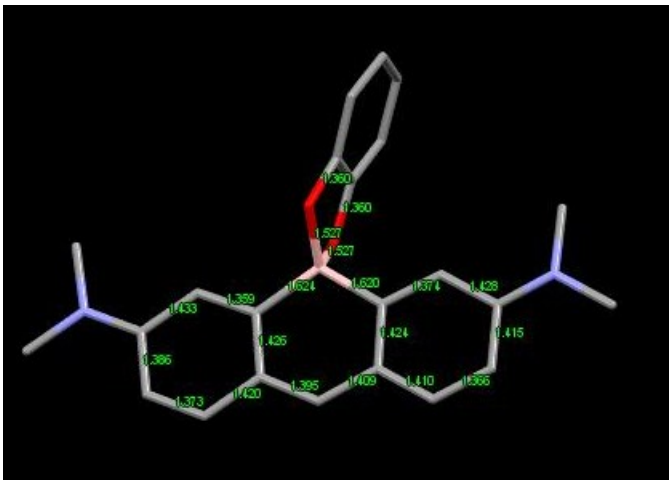

Fig. S4 Detailed structure data of JS-R/CA complex based on the X-ray result (bond length in Å)

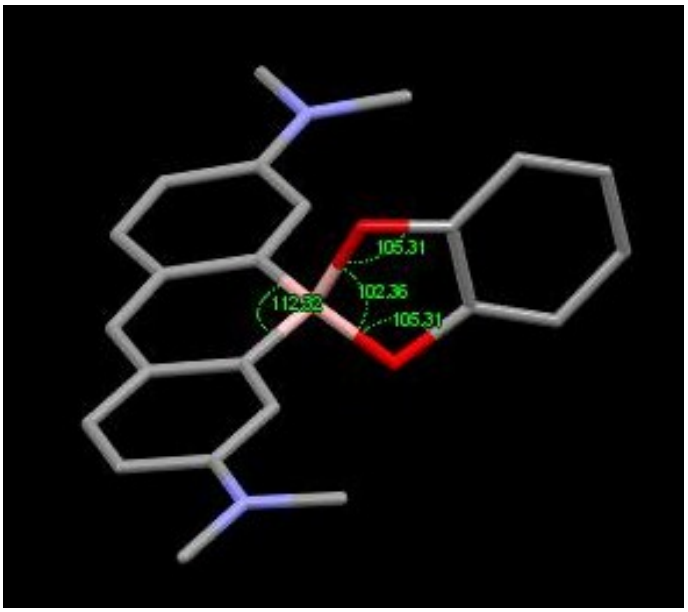

Fig. S5 Detailed structure data of JS-R/CA complex based on the X-ray result (torsion angle in °)

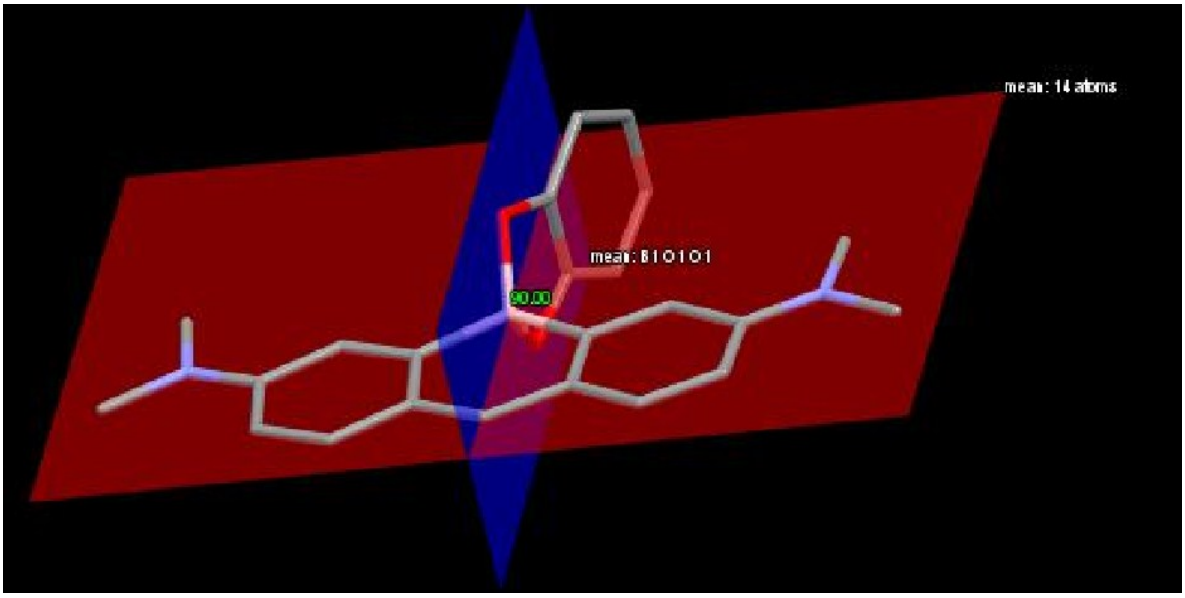

Fig. S6 Detailed structure data of JS-R/CA complex based on the X-ray result (dihedral angle in °)

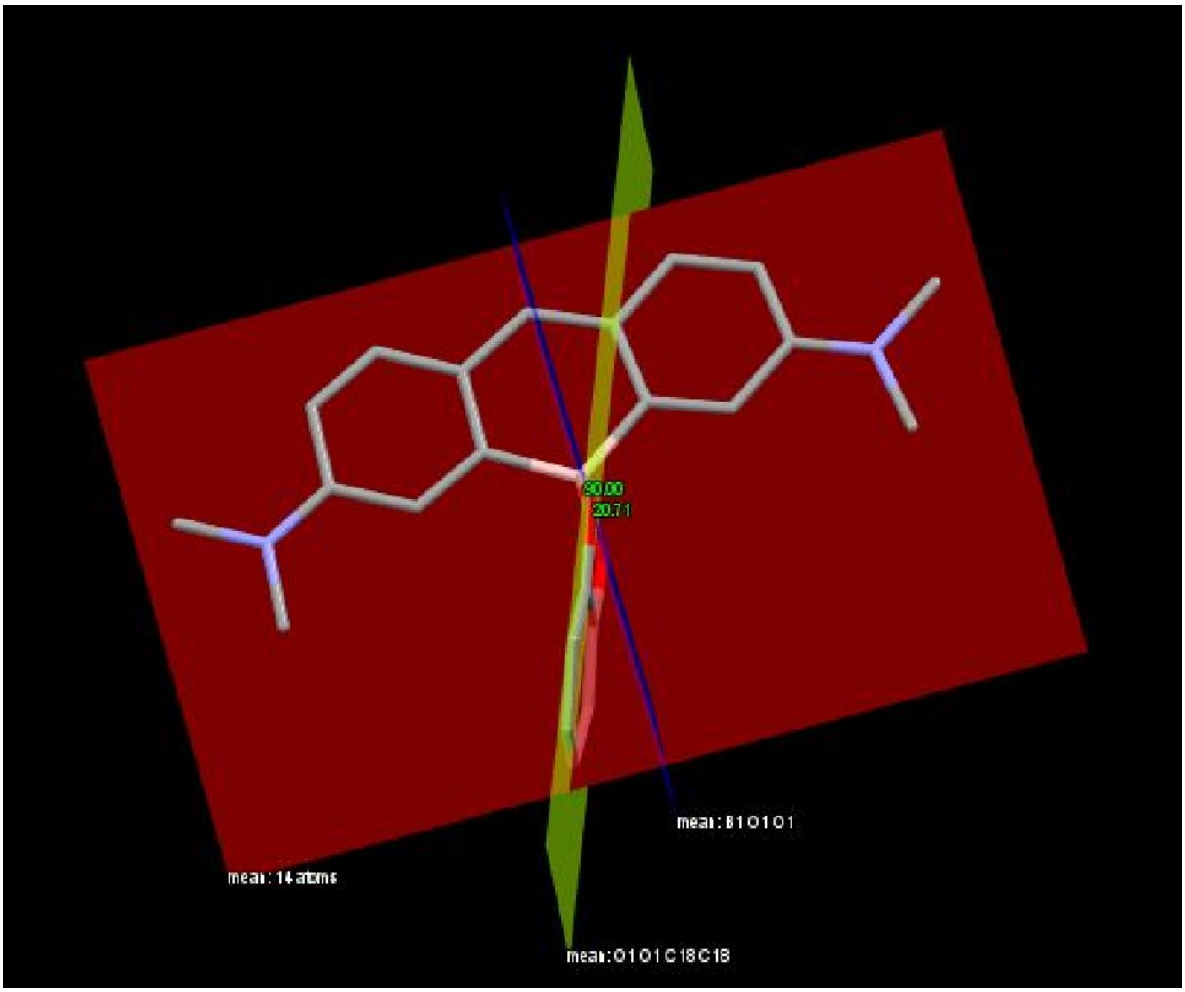

Fig. S7 Detailed structure data of JS-R/CA complex based on the X-ray result (dihedral angle in °)

Table S1 Crystal data and structure refinement for JS-R/CA complex.

Empirical formula	$C_{23}H_{23}BN_2O_2$	
Formula weight	370.24	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Cmca	
Unit cell dimensions	*a* = 7.2732(9) Å	α = 90°.
	b = 18.924(2) Å	β = 90°.
	c = 31.436(4) Å	γ = 90°.
Volume	4326.8(9) $Å^3$	
Z	8	
Density (calculated)	1.137 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	1568	
Crystal size	0.170 x 0.095 x 0.040 mm^3	
Theta range for data collection	1.295 to 27.098°.	
Index ranges	-9<=h<=9, -24<=k<=24, -40<=l<=40	
Reflections collected	23868	
Independent reflections	2576 [R(int) = 0.0263]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2576 / 0 / 161	
Goodness-of-fit on F^2	1.138	
Final R indices [I>2sigma(I)]	R_1 = 0.0655, wR_2 = 0.1889	
R indices (all data)	R_1 = 0.0778, wR_2 = 0.1962	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.318 and -0.275 $e.Å^{-3}$	
CCDC deposition number	1486034	

DFT calculation of PY, JS-R, and complexes

Table S2 Cartesian coordinate of PY

Charge = 1, Multiplicity = 1, Imaginary frequency = 0

C	0.	0.	0.
C	1.33225	-0.20132	0.35222
C	-0.6499	1.19607	0.29637
C	-0.68441	-1.01804	-0.66541
C	-2.01945	-0.78617	-1.00662
C	-1.98152	1.38315	-0.06386
C	-2.71845	0.39329	-0.72198
H	-2.51708	-1.61993	-1.52503
H	-0.11403	2.01142	0.81176
H	-2.44101	2.35679	0.17397
N	-4.03069	0.62801	-1.05929
H	1.89621	0.58873	0.87662
C	1.94479	-1.41086	0.03391
C	1.20467	-2.38852	-0.63239
C	3.27633	-1.65223	0.36492
C	3.87528	-2.8658	0.03862
C	1.8468	-3.59114	-0.93884
C	3.17802	-3.88453	-0.61866
H	3.87328	-0.88116	0.88133
H	4.93768	-2.99626	0.3031
O	-0.11945	-2.23503	-1.00306
H	1.22051	-4.33168	-1.45934
N	3.81568	-5.06453	-0.92167
C	4.26019	-5.75246	0.2369
C	3.14457	-5.91841	-1.82916
H	2.23551	-6.38242	-1.38161
H	2.88743	-5.37647	-2.76755
H	3.82333	-6.74233	-2.14471
H	4.95615	-5.14211	0.85247
H	3.40003	-6.06554	0.87281
H	4.83828	-6.66075	-0.04603
C	-4.84905	0.85623	0.0771
C	-4.6133	-0.29006	-1.96526
H	-3.99688	-0.38184	-2.8883

H	-4.78272	-1.2907	-1.50479
H	-5.59958	0.094	-2.31003
H	-4.89452	-0.0478	0.72744
H	-4.49883	1.71729	0.68681
H	-5.88504	1.11905	-0.23417

Table S3 Cartesian coordinate of JS-R

Charge = 0, Multiplicity = 1, Imaginary frequency = 0

C	-1.35777	-0.0915	0.01574
C	-2.61727	-0.65522	-0.00679
B	-0.01334	-1.0161	0.06204
C	-1.25862	1.33881	0.02239
C	1.34645	-0.09222	0.01101
C	-0.0066	1.9755	0.02656
C	1.24728	1.33868	0.01663
C	2.61226	-0.64939	-0.01417
C	2.43404	2.12428	0.00269
C	3.80984	0.12742	-0.02779
C	3.67838	1.55062	-0.01811
H	-0.00617	3.0646	0.03005
H	2.70803	-1.73003	-0.02187
H	2.35158	3.20782	0.0078
N	5.03463	-0.45797	-0.04939
H	4.55473	2.18374	-0.02756
C	-3.81587	0.12036	-0.02009
H	-2.69392	-1.73481	-0.01733
C	-3.68931	1.54493	-0.00646
N	-5.03898	-0.46775	-0.04533
C	-2.44735	2.1229	0.01376
H	-4.56791	2.1751	-0.01336
H	-2.36743	3.20657	0.02118
O	-0.04768	-1.75762	1.36573
O	-0.07991	-1.93484	-1.11292
C	-5.16517	-1.92434	-0.0571
C	-6.25752	0.3404	-0.064
H	-6.335	0.96787	0.8285
H	-6.29638	0.98434	-0.9472
H	-7.12096	-0.31868	-0.08889
H	-4.69156	-2.35916	-0.94173
H	-4.71401	-2.37113	0.83315
H	-6.21881	-2.18965	-0.07198
C	5.16573	-1.91388	-0.05112
C	6.25052	0.35436	-0.06294
H	6.29029	0.99914	-0.9454

H	6.32292	0.98124	0.83048
H	7.11613	-0.30196	-0.08566
H	6.22018	-2.17578	-0.06589
H	4.71804	-2.35657	0.84322
H	4.6932	-2.35687	-0.93236
H	0.74492	-2.42069	-1.22835
H	0.83596	-2.02512	1.6423

Table S4 Cartesian coordinate of JS-R/Fru

Charge = 0, Multiplicity = 1, Imaginary frequency = 0

C	-1.55142	1.3016	0.08202
C	-2.78418	0.64564	0.1155
B	-0.25643	0.51596	0.02471
C	-1.55377	2.69643	0.10777
C	0.9733	1.39672	-0.04252
C	-0.36043	3.41507	0.06851
C	0.88116	2.7877	-0.0086
C	2.24317	0.82212	-0.12671
C	2.04871	3.54918	-0.0504
C	3.43539	1.55204	-0.1784
C	3.30001	2.94274	-0.12823
H	-0.39954	4.51746	0.09366
H	2.30429	-0.27539	-0.13569
H	1.99728	4.65121	-0.02269
N	4.63149	0.88254	-0.25572
H	4.17568	3.61004	-0.16132
C	-4.02629	1.2873	0.17352
H	-2.77419	-0.45175	0.11148
C	-3.97887	2.68439	0.21268
N	-5.18102	0.5421	0.20835
C	-2.77017	3.3748	0.17603
H	-4.89439	3.29469	0.26157
H	-2.79295	4.47794	0.20011
O	-0.14631	-0.31006	1.16283
O	-0.26723	-0.33729	-1.09662
C	-5.35592	-0.23984	-0.9627
C	-6.35739	1.24131	0.5688
H	-6.21967	1.77685	1.53557
H	-6.69148	1.94739	-0.22606
H	-7.18522	0.51928	0.74897
H	-5.4805	0.40628	-1.86225
H	-4.50856	-0.93749	-1.13996
H	-6.25539	-0.88871	-0.86727
C	4.78187	0.21249	-1.49698
C	5.78043	1.63136	0.09271
H	6.03752	2.40059	-0.6714

H	5.65471	2.10512	1.09287
H	6.65494	0.94981	0.19188
H	5.69536	-0.42356	-1.48479
H	3.93593	-0.47641	-1.71228
H	4.86391	0.93771	-2.3393
C	-0.45014	-1.66844	-0.68605
C	-0.24195	-1.6585	0.79142
O	1.04969	-2.16908	0.99979
C	-1.2303	-2.36715	1.67467
C	0.65756	-2.51164	-1.29776
H	-1.47342	-1.97942	-0.99422
H	1.38271	-1.91934	-1.90806
C	1.29172	-3.08859	-0.04045
O	0.0737	-3.57147	-2.0256
H	-0.91575	-2.43822	2.74222
H	-2.20261	-1.83706	1.79414
O	-1.50628	-3.66522	1.19681
H	-2.13532	-4.0831	1.79691
H	0.46929	-3.57951	-2.90316
C	2.77733	-3.32587	-0.16334
H	0.79481	-4.04107	0.2566
H	3.0411	-3.98961	-1.01982
H	3.38932	-2.4239	-0.395
O	3.27603	-3.92892	1.01114
H	4.23298	-4.01443	0.92404

Table S5 Cartesian coordinate of JS-R/CA

Charge = 0, Multiplicity = 1, Imaginary frequency = 0

B	3.6366	6.4818	11.9994
C	3.6366	5.1876	15.7542
C	3.6366	6.0123	14.5822
H	3.6366	6.9546	14.6995
C	3.6366	5.5266	13.3131
C	3.6366	5.6316	10.6207
C	3.6366	6.2415	9.389
H	3.6366	7.1911	9.3616
C	3.6366	5.5349	8.1476
C	3.6366	4.1213	8.2145
H	3.6366	3.6088	7.4158
C	3.6366	3.4945	9.4286
H	3.6366	2.5453	9.4559
C	3.6366	4.2081	10.6452
C	3.6366	3.532	11.8819
H	3.6366	2.5831	11.8482
C	3.6366	4.1101	13.1516
C	3.6366	3.2871	14.3084
H	3.6366	2.3428	14.2028
C	3.6366	3.8132	15.5769
H	3.6366	3.236	16.331
C	3.6366	7.1135	17.232
H	3.1551	7.5677	16.5102
H	4.5603	7.439	17.2647
H	3.1944	7.299	18.0851
C	3.6366	4.854	18.1845
H	3.9952	5.365	18.9402
H	4.1952	4.0649	18.0285
H	2.7202	4.572	18.3869
C	3.6366	7.6112	6.8631
C	3.6366	5.452	5.6984
H	2.7558	5.047	5.5547
H	4.3196	4.7499	5.7245
H	3.8344	6.0727	4.9669
C	2.9398	8.6301	11.5757
C	2.2292	9.7303	11.1529

H	1.2794	9.7345	11.1692
C	2.9486	10.8419	10.698
H	2.4802	11.6061	10.3865
N	3.6366	5.6904	16.9893
N	3.6366	6.1747	6.9602
O	2.4467	7.4392	12.0104
H	4.5538	7.9443	6.9505
H	3.2737	7.88	5.9948
H	3.0824	7.9859	7.5792
C	4.3334	8.6301	11.5757
C	5.044	9.7303	11.1529
H	5.9938	9.7345	11.1692
C	4.3246	10.8419	10.698
H	4.793	11.6061	10.3865
O	4.8265	7.4392	12.0104

Fluorescence and absorption spectra

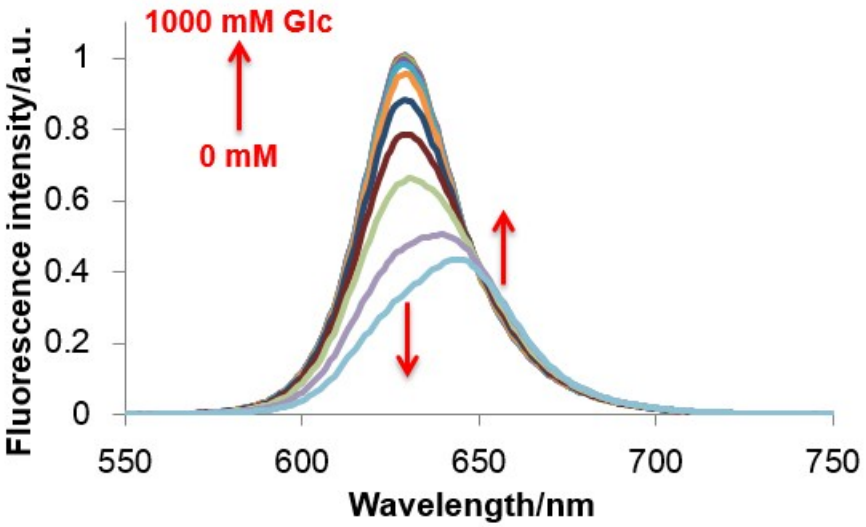

Fig. S8 Fluorescence spectra of JS-R (6.3 μM in 10 mM HEPES buffer at pH 7.4, excited with 611 nm) in the presence and absence of Glc (0, 10, 20, 50, 100, 200, 500, 1000 mM).

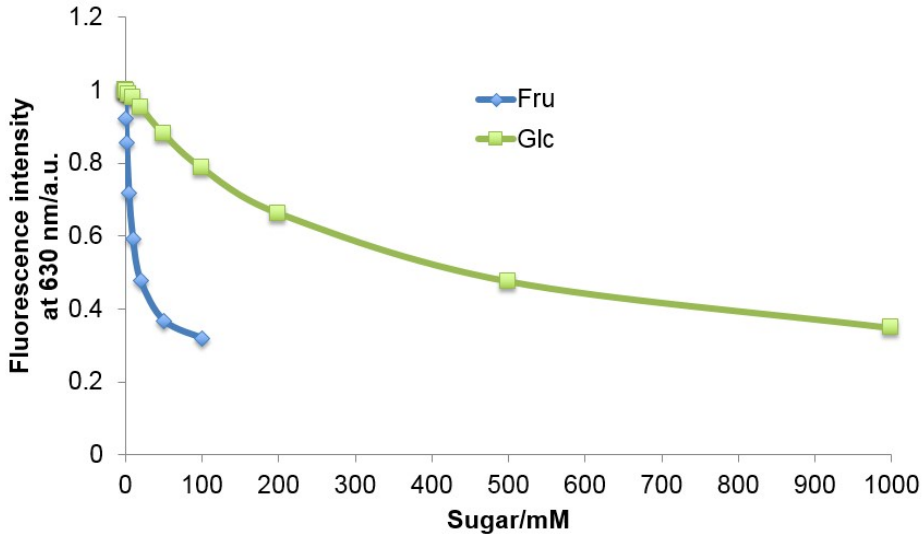

Fig. S9 Titration curve of fluorescence intensity at 630 nm of JS-R (6.3 μM in 10 mM HEPES buffer at pH 7.4, excited with 611 nm) against sugar concentration.

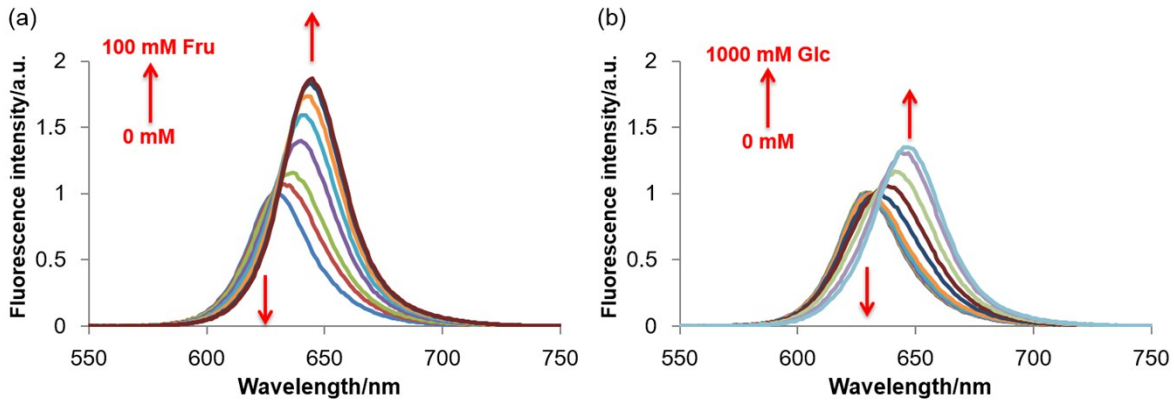

Fig. S10 Fluorescence spectra of JS-R (6.3 μM in 10 mM HEPES buffer at pH 7.4, excited with 632 nm) (a) The effect for Fru (0, 1, 2, 5, 10, 20, 50, 100 mM), (b) The effect for Glc (0, 10, 20, 50, 100, 200, 500, 1000 mM).

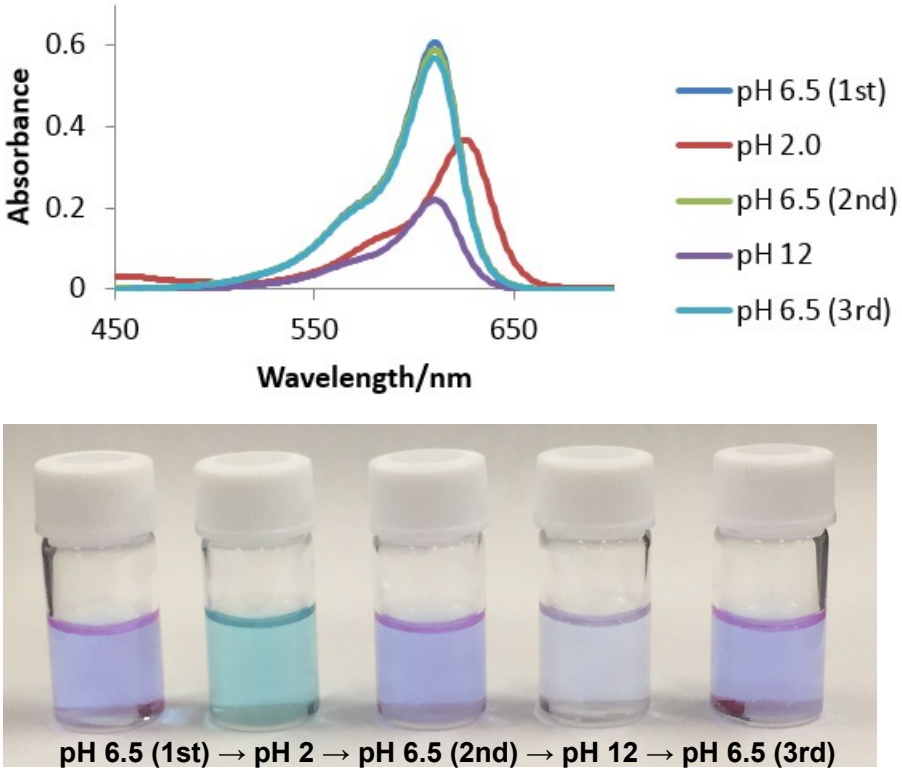

Fig. S11 Reversible pH response of JS-R. The solution of pH 6.5 (1st) was JS-R (5 μM) in water. Small amounts of 1 M HCl and 1 M NaOH were added to the solution to vary its pH successively, and recorded absorption spectra and appearance at each pH. The absorbance of pH 6.5 (2nd) and pH 6.5 (3rd) slightly decreased due to the adding of small amounts of 1 M HCl and 1M NaOH.

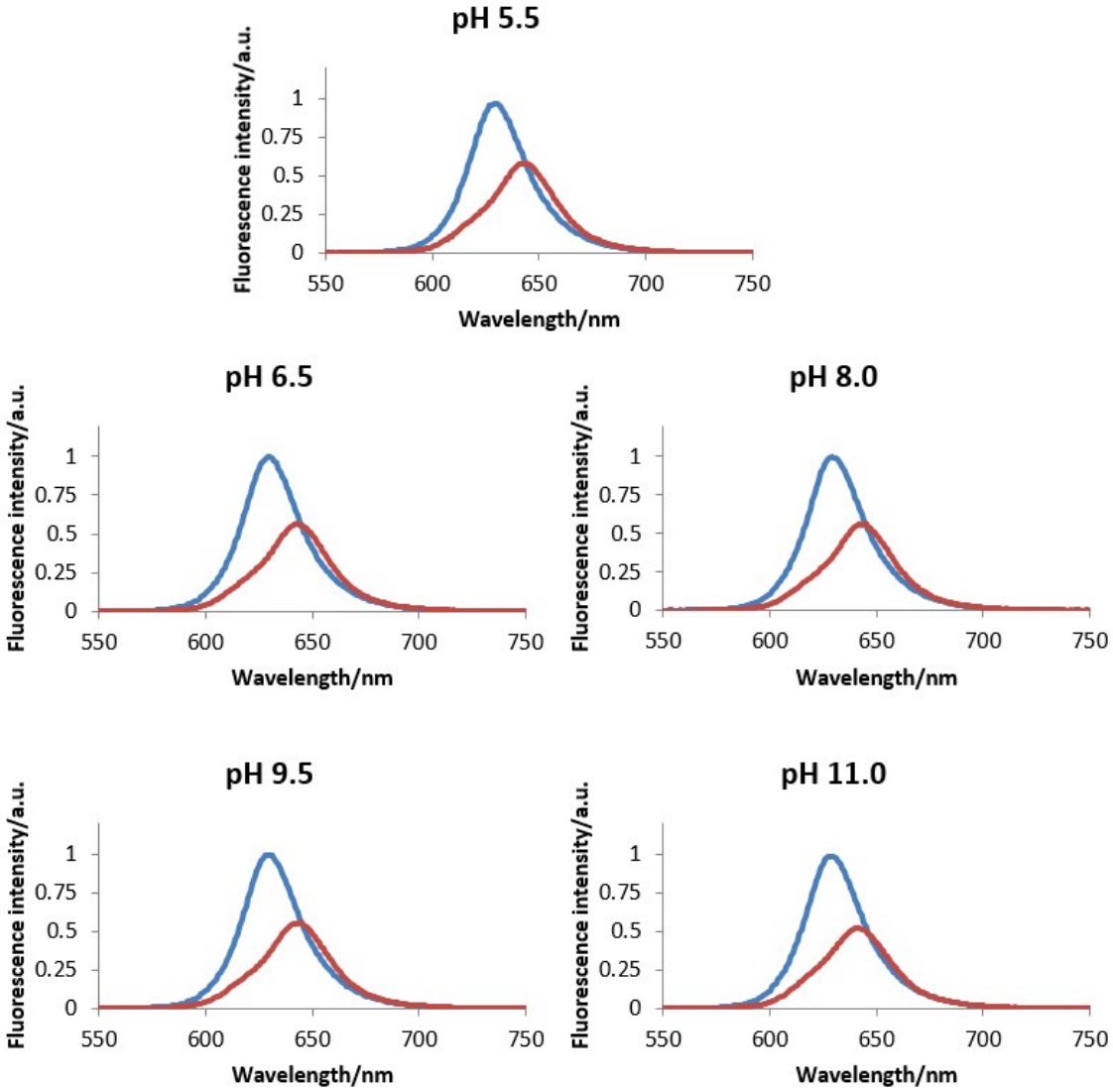

Fig. S12 Fluorescent spectra of JS-R in various pH without sugar (blue) and with 50 mM fructose (red).

References

Complete Reference 17:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.