Supporting Information

Molecular Design of Bioorthogonal Probes and Imaging Reagents Derived from Photofunctional Transition Metal Complexes

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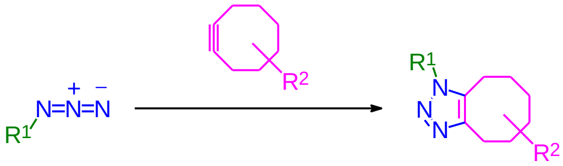
Table S1. Photophysical data of various complexes in degassed solutions at 298 K.

Complex	Solvent	λ_{em}/nm	τ_o/μs	Φ_{em}	I/I_o[a]	Ref.
1a[b]	CH_3OH	610	0.091	0.020	–	1
1b[b]	CH_3OH	551 sh, 595	0.16	0.031	–	1
1c[b]	CH_3OH	514 sh, 553	1.78 (43%), 0.48 (57%)	0.20	–	1
2a[c]	CH_3CN	545	1.24	0.11	–	2
2b[c]	CH_3CN	485 sh, 512	4.57	0.03	–	2
2c[c]	CH_3CN	556	4.20	0.09	–	2
3a[d]	Buffer[e]	605	0.74	0.05	–	3
3b[d]	Buffer[e]	598	0.81	0.07	–	3
4a[c]	CH_3CN	523	1.80	0.003	181.1	4
4b[c]	CH_3CN	548	4.21	0.020	15.6	4
5a[c]	CH_3CN	523	1.70	0.003	145.1	4
5b[c]	CH_3CN	556	4.21	0.022	8.0	4
6a[c]	CH_3CN	528	1.75	0.011	95.5	4
6b[c]	CH_3CN	546	6.08	0.021	35.3	4
7a[b]	Buffer[f]	520	0.86	0.006	25.7	5
7b[b]	Buffer[f]	523 (max), 561, 604 sh	2.57	0.009	19.5	5
7c[b]	Buffer[f]	593 (max), 644, 705 sh	2.90	0.004	121.9	5
7d[b]	Buffer[f]	650	0.07	< 0.001	79.9	5
8a[b]	Buffer[f]	456, 488 sh, 550 (max)	0.31	0.0023	36.6	6
8b[b]	Buffer[f]	484, 513 (max)	1.17	0.0001	96.1	6
8c[b]	Buffer[f]	592	0.24	0.0025	23.1	6

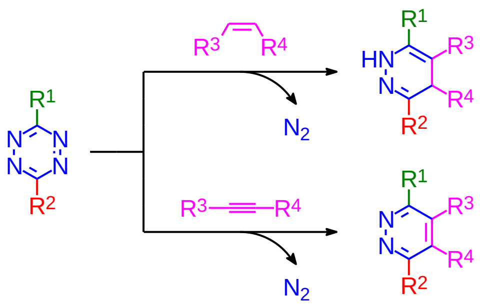
9a[b]	Buffer[f]	579	0.12	0.0006	60.5	7
9b[b]	Buffer[f]	557, 595 sh	2.13	0.014	28.8	7
9c[b]	Buffer[f]	652	0.03	0.0002	135.0	7
10a[d]	Buffer[g]	611	0.641	0.004	9.53	8
10b[d]	Buffer[g]	650	0.523	0.003	7.10	8
10c[d]	Buffer[g]	602	1.030	0.006	10.24	8
10d[d]	Buffer[g]	619	2.836	0.018	5.77	8
10e[d]	Buffer[e]	610	0.685	0.006	3.89	8
11a[b]	Buffer[h]	526	0.36	0.15	1.1	9
11b[b]	Buffer[h]	588	0.11	0.027	7.9	9
11c[b]	Buffer[h]	656	0.03	0.0030	2.5	9

[a] I_o and I are the emission intensities of the complexes in the absence and presence of bicyclo[6.1.0]non-4-yn-9-ylmethanol (BCN-OH) in aerated solutions. Readers are refered to the original references for more details of the reaction conditions. [b] Excitation at 350 nm. [c] Excitation at 355 nm. [d] Excitation at 455 nm. [e] Potassium phosphate buffer (50 mM, pH 7.4)/CH_3OH (4:1, *v*/*v*). [f] Potassium phosphate buffer (50 mM, pH 7.4)/CH_3OH (7:3, *v*/*v*). [g] Potassium phosphate buffer (50 mM, pH 7.4)/DMSO (9:1, *v*/*v*). [h] Potassium phosphate buffer (50 mM, pH 7.4)/DMSO (7:3, *v*/*v*).

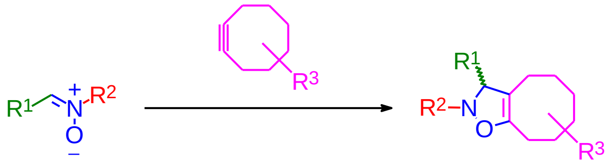
Scheme S1. Strain-promoted alkyne–azide cycloaddition (SPAAC) reaction of an azide with a strained alkyne to afford a triazole derivative.



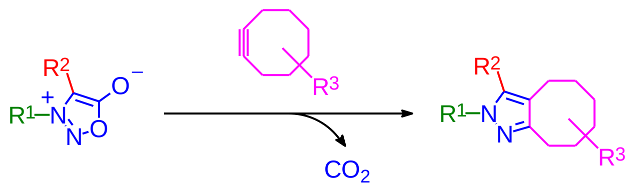
Scheme S2. Inverse Electron-Demand Diels–Alder (IEDDA) cycloaddition reactions of 1,2,4,5-tetrazine with an alkene and alkyne to afford a dihydropyridazine and pyridazine derivative, respectively.



Scheme S3. Strain-promoted alkyne–nitrone cycloaddition (SPANC) reaction of a nitrone with a strained alkyne to afford an isoxazoline derivative.



Scheme S4. Strain-promoted sydnone–alkyne cycloaddition (SPSAC) reaction of a sydnone with a strained alkyne to afford a pyrazole derivative.



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