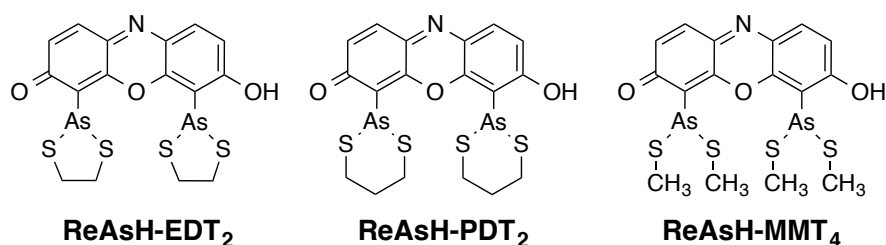


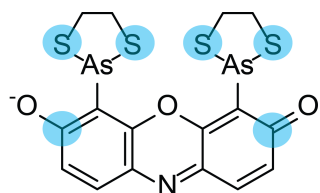
## Rotamer-restricted fluorogenicity of the bis-arsenical ReAsH

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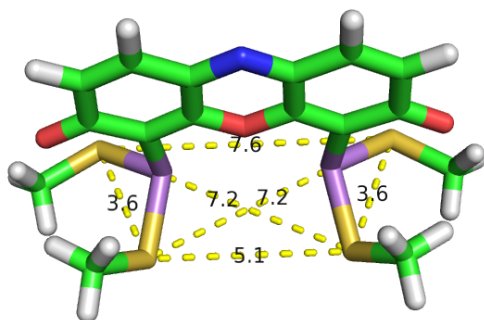
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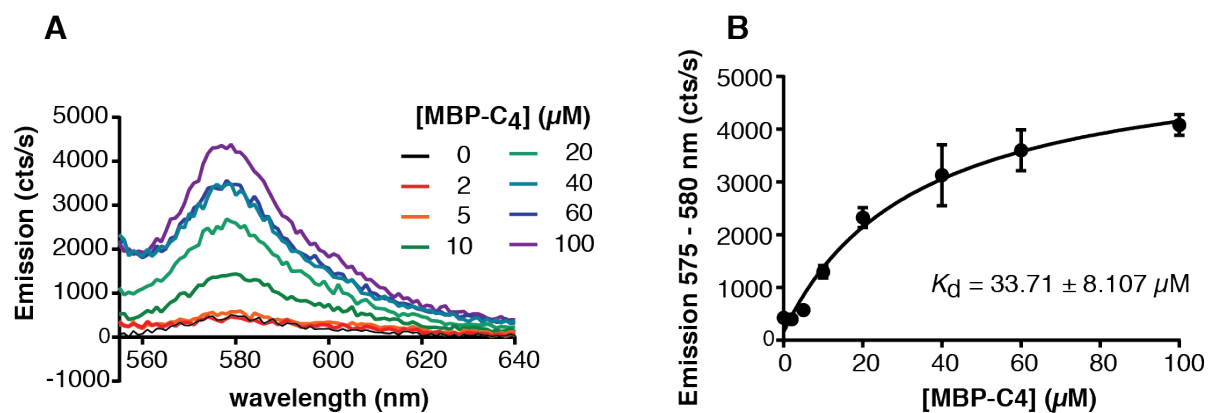
**Figure S1.** Structures of bis-arsenicals ReAsH-EDT<sub>2</sub>, ReAsH-PDT<sub>2</sub>, and ReAsH-MMT<sub>4</sub>.



**Figure S2.** Structure of ReAsH-EDT<sub>2</sub> illustrating the atoms frozen during minimization of the minimum energy quenched structure ( $\Omega = -160^\circ$ ,  $\Omega' = 51^\circ$ ). Atoms highlighted in blue were frozen during the relaxation. The resulting structure remained quenched.



**Figure S3.** Minimized structure of ReAsH-MMT<sub>4</sub> illustrating the 6 interatomic distances ( $D_{\text{ideal}}$ ) used to evaluate Cys<sub>4</sub> motifs in previously studied target proteins p53, EmGFP, and CRABP I. The deviation from this geometry was determined using Equation 1.



**Figure S4. Evaluating the affinity of ReAsH for MBP-C4.** (A) Representative emission spectra of 100 nM ReAsH-EDT<sub>2</sub> as a function of [MBP-C4]. (B) A plot of the average emission between 575 nm and 585 nm of 100 nM ReAsH-EDT<sub>2</sub> as a function of [MBP-C4]. Data was fit as described under Methods.

### Coordinates of minimized structures

#### ReAsH-EDT<sub>2</sub>:

C	3.55204	3.14331	0.01698
C	2.38786	3.80525	0.04164
C	1.14177	3.09915	0.03533
C	1.18311	1.67493	0.01883
C	2.348	0.9472	0.00841
C	3.60951	1.67969	-0.01468
C	-1.18311	1.67493	0.01883
C	-1.14178	3.09915	0.03533
C	-2.38787	3.80525	0.04163
H	-2.34946	4.87961	0.06013
C	-3.55205	3.1433	0.01697
C	-3.60951	1.67968	-0.01468
C	-2.348	0.94719	0.00841
H	4.49424	3.6602	0.01435
H	2.34945	4.87961	0.06013
H	-4.49425	3.66019	0.01434
O	4.69826	1.12121	-0.06945
O	0.	1.03393	0.01342
N	0.	3.75029	0.04554
As	2.1934	-0.96448	-0.0176
As	-2.1934	-0.96448	-0.01761
S	3.57872	-1.61181	1.65125

S	3.58266	-1.66758	-1.64264
S	-3.57869	-1.61182	1.65126
S	-3.58268	-1.66758	-1.64263
C	4.80735	-2.55938	0.67686
C	5.10736	-1.91755	-0.66931
C	-4.80735	-2.55937	0.67688
C	-5.10737	-1.91752	-0.66928
O	-4.69826	1.1212	-0.06946
H	4.44615	-3.56955	0.54717
H	5.7343	-2.58022	-1.25395
H	5.59667	-0.96759	-0.54487
H	5.70782	-2.59132	1.27824
H	-5.70781	-2.5913	1.27828
H	-4.44617	-3.56954	0.54718
H	-5.59666	-0.96756	-0.54482
H	-5.73433	-2.58019	-1.25392

**ReAsH-PDT<sub>2</sub>:**

C	3.55124	3.21015	-0.00004
C	2.38481	3.86759	-0.00018
C	1.14051	3.16024	-0.00013
C	1.18528	1.73231	0.00009
C	2.34931	1.01203	0.00014
C	3.60992	1.7451	0.00018
C	-1.18549	1.73238	0.00004
C	-1.14063	3.16031	-0.00017
C	-2.38489	3.86775	-0.00022
H	-2.3371	4.94239	-0.00032
C	-3.55134	3.21036	-0.00012
C	-3.61012	1.74529	-0.00001
C	-2.34956	1.01214	0.00009
H	4.49623	3.72189	-0.00005
H	2.33709	4.94223	-0.00033
H	-4.49631	3.72214	-0.0001
O	4.69571	1.18701	0.00046
O	-0.00013	1.08918	0.0002
N	-0.00004	3.81298	-0.00024
As	2.2114	-0.9056	0.00033
As	-2.21143	-0.90547	0.00028
S	3.44121	-1.60027	1.74253
S	3.44047	-1.59991	-1.74254
S	-3.44108	-1.6002	1.74256
S	-3.44031	-1.60038	-1.7425
O	-4.69594	1.18731	0.00003

C	-5.21031	-1.55525	-1.2908
H	-5.53608	-0.52904	-1.25819
H	-5.6907	-2.0491	-2.12925
C	-5.21086	-1.55482	1.2901
H	-5.53638	-0.52854	1.25696
H	-5.69176	-2.04829	2.12848
C	5.21101	-1.55488	1.29005
H	5.5366	-0.52862	1.25735
H	5.69188	-2.04875	2.12821
C	5.21044	-1.55459	-1.29095
H	5.53616	-0.52836	-1.25832
H	5.69082	-2.0484	-2.12944
C	-5.5925	-2.2792	-0.00032
H	-5.18802	-3.28676	-0.00007
H	-6.67905	-2.36899	-0.00055
C	5.59283	-2.27869	-0.00061
H	6.67942	-2.36808	-0.00088
H	5.1888	-3.28645	-0.00077

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