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Supporting Information

Theoretical Study of the *cis-trans* Isomerization Mechanism of a Pendant Metal-bound Azobenzene

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Table S1. The absorption band energies of the *trans* and *cis* $Re(CO)_3$-AB.

methods	*trans*					*cis*				
	B3LYP	CAM-B3LYP	M06	M06-2X	PBE0	B3LYP	CAM-B3LYP	M06	M06-2X	PBE0
λ_{max} (nm)	541.56	451.34	452.49	489.98	512.56	531.05	446.90	518.53	442.77	446.79

Table S2. The test for different solvents in the current paper. (Bond length and bond angle are in Angstroms and Degrees)

	cis					*trans*					
solvent	N_1-N_2	$C_5N_1N_2$	$N_1N_2C_3$	$C_5N_1N_2C_3$	E/a.u.	N_1-N_2	$C_5N_1N_2$	$N_1N_2C_3$	$C_5N_1N_2C_3$	E/a.u.	ΔE_{zpe}/eV
gas phase	1.244	124.4	124.3	-9.1	-1793.080656	1.254	114.9	115.3	-179.7	-1793.104852	0.64
hexane	1.244	124.4	124.1	-9.6	-1793.137890	1.253	115.2	115.6	-179.7	-1793.160777	0.62
THF	1.245	124.2	123.9	-9.9	-1793.151971	1.254	115.3	115.7	-179.8	-1793.173843	0.59
acetonitrile	1.245	124.1	123.9	-10.0	-1793.157379	1.254	115.4	115.7	-179.9	-1793.178910	0.58
water	1.245	124.1	123.8	-10.0	-1793.158249	1.254	115.4	115.8	-180.0	-1793.179727	0.58

Note: ΔE is the relative energy with respect to the *trans*-S_0.

Table S3. The test for different solvents for TS-inv-1. (Bond length and bond angle are in Angstroms and Degrees)

	TS-inv-1			
solvent	N_1-N_2	$C_5N_1N_2$	$N_1N_2C_3$	E_{zpe}/a.u.
gas phase	1.221	117.1	179.6	-1792.731271
hexane	1.220	117.3	179.7	-1792.741411
THF	1.219	117.6	179.9	-1792.802740
acetonitrile	--	--	--	--
water	1.220	117.6	179.6	-1792.761667

Fig. S1 Simulated absorption spectra of the *trans* $Re(CO)_3$-AB based on the various functionals.

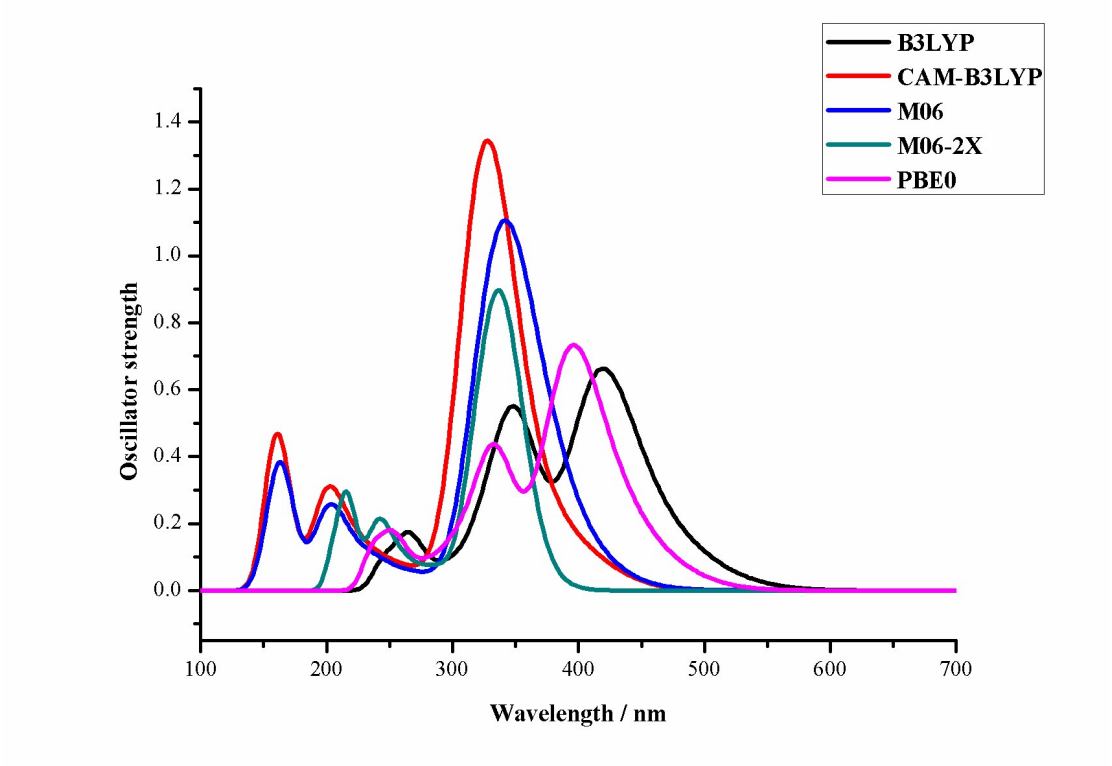

Fig. S2 Potential energy profiles in the excited states for $Re(CO)_3$-AB along the $C_5N_1N_2$ inversion coordinate.