Boranil and related NBO Dyes: Insights From Theory:

Supporting Information

Siwar Chibani,[†] Azzam Charaf-Eddin,[†] Boris Le Guennic,[*,‡] and Denis Jacquemin[*,†,¶]

Laboratoire CEISAM - UMR CNR 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France, Institut des Sciences Chimiques de Rennes, CNRS-Université de Rennes 1, 1 Av. du General Leclerc, 35042 Rennes Cedex, France, and Institut Universitaire de France, 103, bd Saint-Michel, F-75005 Paris Cedex 05, France.

E-mail: Boris.leguennic@univ-rennes1.fr; Denis.Jacquemin@univ-nantes.fr

[*]To whom correspondence should be addressed
[†]CEISAM, Nantes
[‡]ISCR, Rennes
[¶]IUF, Paris

Experimental and theoretical data

Table S-I: The experimental 0-0 energies for dyes shown in Schemes 2 and 3. All values are in eV.

Dye	Solvent	0-0	Ref.
I	Dichloromethane	2.505	1
II	Dichloromethane	2.463	1
III	Toluene	3.322	2
IV	Toluene	3.122	2
V	Toluene	3.180	2
VI	Dichloromethane	2.705	3
VII	Dichloromethane	2.822	3
VIII	Toluene	2.983	4
IX	Toluene	2.959	4
X	Toluene	2.760	4
XI	Toluene	2.436	4
XII	Toluene	2.688	4
XIII	Toluene	2.776	4
XIV	Toluene	2.625	4
XV	Toluene	2.674	4
XVI	Toluene	3.199	2
XVII	Toluene	3.423	2
XVIII	Toluene	3.414	2
XIX	Toluene	3.157	2
XX	Toluene	3.083	2
XXI	Acetonitrile	2.401	5
XXII	Acetonitrile	2.384	5
XXIII	Acetonitrile	2.370	5
XXIV	Dichloromethane	2.943	6
XXV	Dichloromethane	2.398	6

Table S-II: Theoretical best estimates of the experimental 0-0 energies for the ten first dyes. All values are in eV and have been obtained from Eq. (5) in the equilibrium limit (LR,eq).

Dyes	B3LYP	PBE0	M06	BMK	M06-2X	CAM-B3LYP	ωB97X-D	ωB97
I	2.254	2.368	2.432	2.616	2.720	2.744	2.770	2.975
II	2.291	2.385	2.410	2.523	2.576	2.639	2.653	2.838
III	3.267	3.390	3.359	3.576	3.637	3.607	3.613	3.772
IV	3.013	3.125	3.077	3.307	3.357	3.351	3.372	3.552
V	3.223	3.337	3.305	3.532	3.502	3.533	3.548	3.688
VI	2.524	2.618	2.610	2.861	2.854	2.928	2.980	3.194
VII	2.657	2.751	2.743	2.981	2.965	3.033	3.080	3.237
VIII	2.816	2.922	2.897	3.132	3.189	3.206	3.250	3.437
IX	2.981	3.067	2.849	3.244	3.223	3.286	3.296	3.466
X	2.394	2.727	2.736	3.057	3.076	3.128	3.189	3.339

Table S-III: Theoretical best estimates of the experimental 0-0 energies for the ten first dyes. All values are in eV and have been obtained from Eq. (5) in the non-equilibrium limit (LR,neq).

Dyes	B3LYP	PBE0	M06	BMK	M06-2X	CAM-B3LYP	ωB97X-D	ωB97
I	2.280	2.404	2.475	2.683	2.795	2.822	2.851	3.072
II	2.110	2.463	2.491	2.609	2.668	2.731	2.747	2.944
III	3.271	3.394	3.363	3.581	3.643	3.612	3.618	3.777
IV	3.019	3.131	3.083	3.292	3.362	3.356	3.380	3.557
V	3.230	3.345	3.313	3.539	3.510	3.541	3.557	3.696
VI	2.724	2.819	2.849	3.081	3.079	3.063	3.128	3.327
VII	2.785	2.880	2.840	3.124	3.071	3.163	3.212	3.376
VIII	2.823	2.929	2.903	3.139	3.196	3.213	3.256	3.443
IX	2.989	3.075	3.036	3.251	3.231	3.294	3.303	3.473
X	2.387	2.731	2.743	3.064	3.084	3.135	3.196	3.347

Table S-IV: Theoretical best estimates of the experimental 0-0 energies for the ten first dyes. All values are in eV and have been obtained from Eq. (6) in the equilibrium limit (SS,eq).

Dyes	B3LYP	PBE0	M06	BMK	M06-2X	CAM-B3LYP	ωB97X-D	ωB97
I	1.128	1.405	1.633	2.229	2.506	2.574	2.642	2.949
II	2.219	2.384	2.430	2.579	2.663	2.733	2.740	2.956
III	3.272	3.415	3.385	3.647	3.721	3.689	3.696	3.868
IV	3.073	3.194	3.140	3.389	3.443	3.435	3.456	3.643
V	3.313	3.437	3.418	3.647	3.619	3.656	3.670	3.810
VI	2.526	2.641	2.636	2.914	2.928	2.975	3.026	3.282
VII	2.824	2.960	2.909	3.251	3.233	3.298	3.342	3.501
VIII	2.821	2.954	2.929	3.204	3.280	3.283	3.339	3.545
IX	3.104	3.195	1.926	3.385	3.365	3.426	3.435	3.609
X	0.901	1.660	1.692	2.993	3.167	3.225	3.304	3.468

Table S-V: Theoretical best estimates of the experimental 0-0 energies for the first ten dyes. All values are in eV and have been obtained from Eq. (6) in the non-equilibrium limit (SS,neq).

Dyes	B3LYP	PBE0	M06	BMK	M06-2X	CAM-B3LYP	ωB97X-D	ωB97
I	1.067	1.349	1.579	2.207	2.487	2.558	2.629	2.941
II	0.480	2.314	2.409	2.562	2.649	2.721	2.728	2.947
III	3.271	3.415	3.384	3.647	3.720	3.689	3.696	3.868
IV	3.073	3.194	3.140	3.369	3.443	3.435	3.458	3.643
V	3.312	3.437	3.417	3.647	3.619	3.656	3.671	3.810
VI	2.535	2.665	2.700	2.975	2.993	2.956	3.023	3.282
VII	2.806	2.949	2.862	3.254	3.200	3.295	3.342	3.507
VIII	2.819	2.953	2.927	3.202	3.280	3.283	3.338	3.545
IX	3.104	3.195	3.145	3.384	3.365	3.426	3.434	3.609
X	0.806	1.645	1.681	2.988	3.166	3.225	3.302	3.468

Table S-VI: Theoretical best estimates of the experimental AFCP energies, AFCP (SS,neq), for the ten first dyes. All values are in eV and have been obtained from Eq. (7).

Dyes	B3LYP	PBE0	M06	BMK	M06-2X	CAM-B3LYP	ωB97X-D	ωB97
I	1.492	1.780	2.016	2.399	2.598	2.653	2.707	2.978
II	2.540	2.812	2.814	2.605	2.693	2.758	2.767	2.986
III	3.274	3.417	3.387	3.649	3.722	3.691	3.697	3.869
IV	3.075	3.195	3.141	3.390	3.444	3.435	3.457	3.643
V	3.316	3.439	3.419	3.649	3.620	3.657	3.671	3.810
VI	2.701	2.822	2.827	3.106	3.023	3.133	3.098	3.280
VII	3.292	3.239	2.917	3.277	3.253	3.313	3.356	3.518
VIII	2.832	2.966	2.941	3.213	3.282	3.284	3.339	3.546
IX	3.105	3.196	1.919	3.385	3.365	3.427	3.435	3.610
X	0.914	1.678	1.712	3.020	3.172	3.231	3.306	3.469

Table S-VII: Dipole moment of the ground and excited states for **X**. All values are in Debye.

	Toluene			Acetonitrile		
Functional	μ^{GS}	μ^{ES}	$\Delta\mu$	μ^{GS}	μ^{ES}	$\Delta\mu$
B3LYP	13.7	32.3	18.6	16.5	40.5	24.0
PBE0	14.0	29.6	15.6	16.2	37.0	20.8
M06	14.0	28.2	14.2	16.1	30.6	20.1
BMK	14.2	24.6	10.4	16.5	30.6	14.1
M06-2X	13.4	20.2	6.8	15.4	24.1	8.7
CAM-B3LYP	13.4	19.7	6.3	15.4	23.7	8.3
ωB97X-D	13.3	18.4	5.1	15.2	21.8	6.6
ωB97	12.7	16.8	4.1	14.5	19.3	4.8

Table S-VIII: Statistical analysis for the nine first dyes (that is **X** removed from the statistics) in Scheme 2 obtained from comparison between experimental and theoretical 0-0 energies. MSE, MAE and SD are in eV.

Functional	Method	MSE	MAE	SD	R^2
B3LYP	0-0 (LR,eq)	-0.115	0.129	0.099	0.966
	0-0 (LR,neq)	-0.092	0.114	0.134	0.929
	0-0 (SS,eq)	-0.198	0.260	0.462	0.720
	0-0 (SS,neq)	-0.399	0.461	0.763	0.797
	AFCP (SS,neq)	-0.048	0.232	0.403	0.572
PBE0	0-0 (LR,eq)	-0.011	0.085	0.101	0.972
	0-0 (LR,neq)	0.042	0.077	0.086	0.951
	0-0 (SS,eq)	-0.053	0.230	0.411	0.747
	0-0 (SS,neq)	-0.066	0.240	0.429	0.752
	AFCP (SS,neq)	0.090	0.254	0.336	0.596
M06	0-0 (LR,eq)	-0.042	0.078	0.076	0.967
	0-0 (LR,neq)	0.032	0.065	0.076	0.941
	0-0 (SS,eq)	-0.184	0.274	0.447	0.551
	0-0 (SS,neq)	-0.055	0.176	0.341	0.772
	AFCP (SS,neq)	-0.076	0.274	0.430	0.348
BMK	0-0 (LR,eq)	0.190	0.190	0.091	0.978
	0-0 (LR,neq)	0.249	0.249	0.089	0.933
	0-0 (SS,eq)	0.234	0.304	0.227	0.878
	0-0 (SS,neq)	0.243	0.309	0.235	0.865
	AFCP (SS,neq)	0.290	0.314	0.185	0.875
M06-2X	0-0 (LR,eq)	0.218	0.218	0.074	0.985
	0-0 (LR,neq)	0.277	0.277	0.057	0.969
	0-0 (SS,eq)	0.300	0.300	0.141	0.954
	0-0 (SS,neq)	0.299	0.304	0.142	0.954
	AFCP (SS,neq)	0.326	0.326	0.112	0.960
CAM-B3LYP	0-0 (LR,eq)	0.252	0.252	0.058	0.982
	0-0 (LR,neq)	0.304	0.304	0.051	0.971
	0-0 (SS,eq)	0.334	0.334	0.132	0.927
	0-0 (SS,neq)	0.329	0.329	0.138	0.927
	AFCP (SS,neq)	0.366	0.366	0.113	0.921
ωB97X-D	0-0 (LR,eq)	0.278	0.278	0.051	0.985
	0-0 (LR,neq)	0.332	0.332	0.058	0.962
	0-0 (SS,eq)	0.365	0.365	0.120	0.933
	0-0 (SS,neq)	0.362	0.362	0.124	0.932
	AFCP (SS,neq)	0.385	0.385	0.103	0.933
ωB97	0-0 (LR,eq)	0.455	0.455	0.044	0.983
	0-0 (LR,neq)	0.512	0.512	0.061	0.964
	0-0 (SS,eq)	0.567	0.567	0.077	0.956
	0-0 (SS,neq)	0.566	0.566	0.080	0.954
	AFCP (SS,neq)	0.576	0.576	0.071	0.956

Table S-IX: Theoretical estimates of the experimental 0-0 energies for all tested dyes with the M06-2X functional. All values are in eV.

	Eq. (5)		Eq. (6)		Eq. (7)
Dyes	0-0 (LR,eq)	0-0 (LR,neq)	0-0 (SS,eq)	0-0 (SS,neq)	AFCP (SS,neq)
I	2.720	2.795	2.506	2.487	2.598
II	2.576	2.668	2.663	2.649	2.693
III	3.637	3.643	3.721	3.720	3.722
IV	3.357	3.362	3.443	3.443	3.444
V	3.502	3.510	3.619	3.619	3.620
VI	2.854	3.079	2.928	2.993	3.023
VII	2.965	3.071	3.233	3.200	3.253
VIII	3.189	3.196	3.280	3.280	3.282
IX	3.365	3.231	3.365	3.365	3.365
X	3.167	3.084	3.167	3.166	3.172
XI	2.683	2.692	2.841	2.841	2.841
XII	2.945	2.949	3.014	3.014	3.015
XIII	3.054	3.059	3.158	3.158	3.158
XIV	3.378	3.378	2.590	2.589	2.587
XV	2.859	2.866	2.989	2.989	2.989
XVI	3.473	3.476	3.487	3.486	3.489
XVII	3.710	3.717	3.838	3.838	3.839
XVIII	3.691	3.698	3.804	3.804	3.805
XIX	3.426	3.429	3.421	3.421	3.423
XX	3.351	3.354	3.315	3.315	3.319
XXI	2.551	2.724	2.767	2.764	2.789
XXII	2.522	2.693	2.725	2.722	2.747
XXIII	2.515	2.681	2.709	2.706	2.732
XXIV	3.174	3.316	3.392	3.383	3.417
XXV	2.595	2.670	2.218	2.210	2.350

Table S-X: Adiabatic and zero-point vibrational energies obtained obtained with the (LR,eq) approach. All values are in eV.

Dyes		B3LYP	PBE0	M06	BMK	M06-2X	CAM-B3LYP	ωB97X-D	ωB97
I	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	2.330	2.446	2.499	2.705	2.791	2.814	2.838	3.047
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.077	-0.077	-0.067	-0.089	-0.071	-0.071	-0.068	-0.072
II	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	2.402	2.486	2.522	2.643	2.672	2.719	2.748	2.901
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.111	-0.101	-0.111	-0.119	-0.096	-0.080	-0.095	-0.063
III	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	3.379	3.501	3.468	3.684	3.742	3.709	3.717	3.866
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.112	-0.111	-0.109	-0.108	-0.105	-0.103	-0.104	-0.094
IV	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	3.117	3.228	3.178	3.402	3.455	3.449	3.469	3.646
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.104	-0.103	-0.101	-0.095	-0.098	-0.098	-0.097	-0.094
V	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	3.347	3.453	3.436	3.595	3.601	3.634	3.656	3.777
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.124	-0.116	-0.130	-0.063	-0.099	-0.101	-0.108	-0.089
VI	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	2.620	2.710	2.690	2.909	2.948	3.013	3.070	3.271
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.095	-0.092	-0.080	-0.048	-0.094	-0.084	-0.091	-0.077
VII	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	2.759	2.846	2.822	3.008	3.037	3.115	3.171	3.313
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.102	-0.095	-0.080	-0.027	-0.071	-0.082	-0.091	-0.076
VIII	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	2.895	3.003	2.957	3.197	3.278	3.282	3.332	3.525
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.079	-0.080	-0.060	-0.065	-0.088	-0.076	-0.082	-0.087
IX	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	3.084	3.167	2.956	3.310	3.317	3.381	3.417	3.548
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.103	-0.100	-0.107	-0.066	-0.094	-0.095	-0.122	-0.082
X	$E^{\text{adia}}_{6-311+G(2d,p)}(\text{LR},\text{eq})$	2.466	2.813	2.846	3.081	3.168	3.213	3.271	3.413
	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$	-0.072	-0.086	-0.110	-0.024	-0.092	-0.086	-0.082	-0.074

Table S-XI: Adiabatic and zero-point vibrational energies obtained with the (LR,eq) approach using the M06-2X functional. All values are in eV.

Dyes	$E^{\text{adia}}_{6-311+\text{G(2d,p)}}(\text{LR},\text{eq})$	$\Delta E^{\text{ZPVE}}(\text{LR},\text{eq})$
XI	2.756	-0.074
XII	3.038	-0.093
XIII	3.181	-0.127
XIV	3.471	-0.093
XV	2.954	-0.094
XVI	3.564	-0.092
XVII	3.822	-0.111
XVIII	3.807	-0.115
XIX	3.516	-0.090
XX	3.444	-0.092
XXI	2.629	-0.077
XXII	2.595	-0.073
XXIII	2.593	-0.078
XXIV	3.236	-0.062
XXV	2.648	-0.052

Vibronic shapes

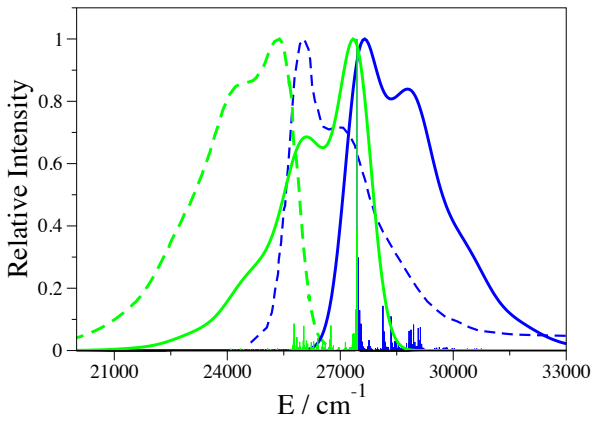

Figure S-1: Comparison between M06-2X (full lines) and experimental (dashed lines) spectra for **V**. The experimental spectra was taken from Ref. 2.

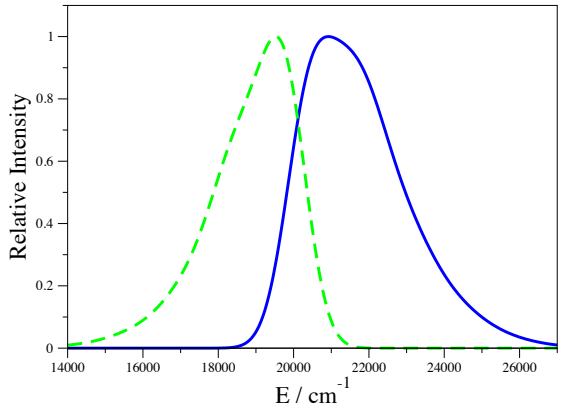

Figure S-2: Absorption (full) and emission spectra (dashed) of **II** computed with M06-2X. The experimental spectra can be found in Ref. 1.

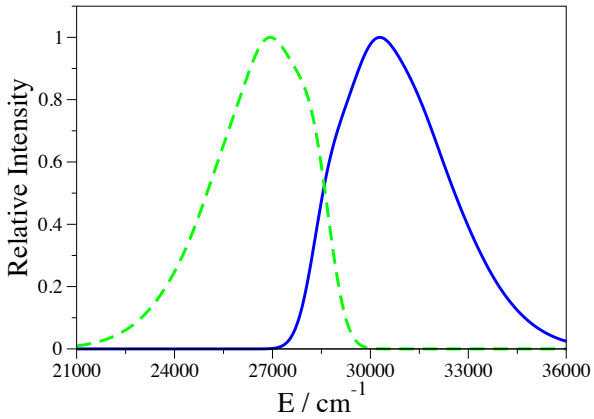

Figure S-3: Absorption (full) and emission spectra (dashed) of **III** computed with M06-2X. The experimental spectra can be found in Ref. 2.

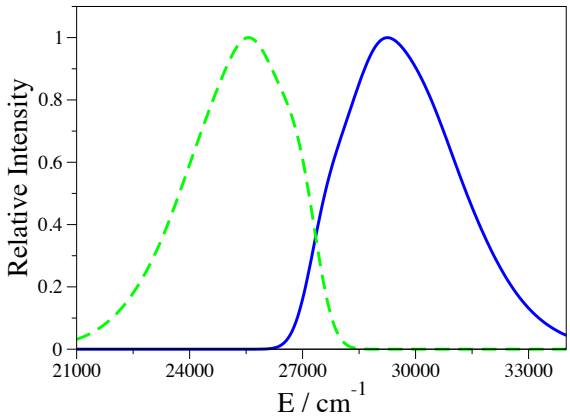

Figure S-4: Absorption (full) and emission spectra (dashed) of **XVI** computed with M06-2X. The experimental spectra can be found in Ref. 2.

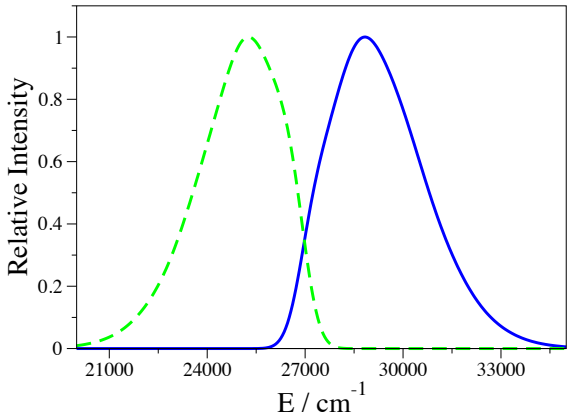

Figure S-5: Absorption (full) and emission spectra (dashed) of **XIX** computed with M06-2X. The experimental spectra can be found in Ref. 2.

Density difference plots

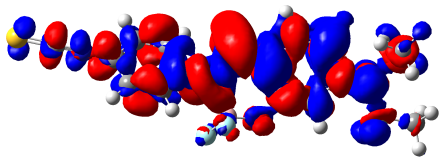

Figure S-6: Density difference plot for **VII**

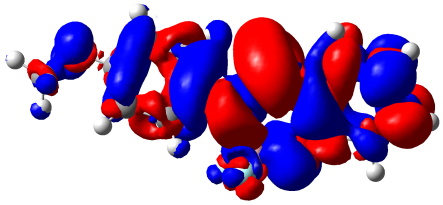

Figure S-7: Density difference plot for **VIII**

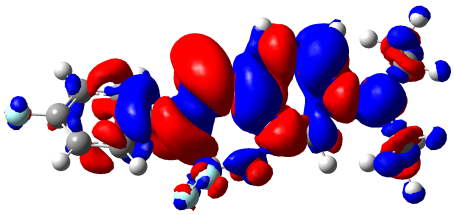

Figure S-8: Density difference plot for **IX**

References

(1) Zhou, Y.; Xiao, Y.; Chi, S.; Qian, X. *Org. Lett.* **2008**, *10*, 633–636.

(2) Massue, J.; Frath, D.; Ulrich, G.; Retailleau, P.; Ziessel, R. *Org. Lett.* **2012**, *14*, 230–233.

(3) Frath, D.; Azizi, S.; Ulrich, G.; Ziessel, R. *Org. Lett.* **2012**, *14*, 4774–4777.

(4) Frath, D.; Azizi, S.; Ulrich, G.; Retailleau, P.; Ziessel, R. *Org. Lett.* **2011**, *13*, 3414–3417.

(5) Singh, R. S.; Yadav, M.; Gupta, R. K.; Pandey, R.; Pandey, D. S. *Dalton Trans.* **2013**, *42*, 1696–1707.

(6) Santra, M.; Moon, H.; Park, M.; lee, T.; Kim, Y. K.; Ahn, K. H. *Chem. Eur. J.* **2012**, *18*, 9886–9893.