Supporting Information

Basis set effect on vertical excitation energies

The effect of the basis set on the predicted vertical excitation energies is examined here. We consider the 6-31+G(d), 6-311+G(d), and aug-cc-pVTZ basis sets with TD-DFT, and only the smaller 6-31+G(d) and 6-311+G(d) basis sets for the correlated wavefunction methods. The smallest *syn*-(H, H) and *anti*-(H, H) bimanes, which make up the core of the different bimane derivatives, are used in this part of the study. The vertical excitation energies of the first allowed excitation of the *syn*-(H, H) and *anti*-(H, H) bimanes are given in Table S1. The lowest allowed transition in the bimanes can be classifed as a $\pi \rightarrow \pi^*$ transition. We only consider the smaller 6-31+G(d) and 6-311+G(d) basis sets for the more expensive correlated wavefunction methods. The cheaper computational cost of TD-DFT allows the inclusion of the large aug-cc-pVTZ basis set here.

Table S1. Vertical excitation energies (eV) of *syn*-(H, H) (**1**) and *anti*-(H, H) (**2**) bimane calculated with various correlated wavefunction methods and TD-DFT. The oscillator strengths for the electronic transitions are given in parentheses.

		SAC-CI	EOM-CCSD [CR-EOM-CCSD(T)]	B3LYP	PBE0	M06	BMK	CAM-B3LYP	M06-2X
1	6-31+G(d)	4.03 (0.3048)	4.07 (0.3180) [3.79]	3.81 (0.1986)	3.89 (0.2129)	3.92 (0.1980)	4.06 (0.2336)	4.11 (0.2320)	4.06 (0.2387)
	6-311+G(d)	4.12 (0.3048)	4.06 (0.3118) [3.76]	3.85 (0.1954)	3.92 (0.2101)	3.96 (0.1966)	4.06 (0.2279)	4.16 (0.2266)	4.06 (0.2318)
	aug-cc-pVTZ	-	-	3.75 (0.1883)	3.82 (0.1993)	3.82 (0.1941)	4.02 (0.2122)	4.06 (0.2164)	4.02 (0.2140)
2	6-31+G(d)	4.19 (0.4306)	4.14 (0.4428) [3.91]	3.99 (0.2660)	4.07 (0.2833)	4.08 (0.2719)	4.24 (0.3290)	4.22 (0.3449)	4.21 (0.3382)
	6-311+G(d)	4.16 (0.4234)	4.13 (0.4327) [3.85]	3.97 (0.2609)	4..06 (0.2781)	4.06 (0.2678)	4.23 (0.3257)	4.22 (0.3380)	4.21 (0.3338)
	aug-cc-pVTZ	-	-	3.93 (0.2444)	4.01 (0.2586)	4.00 (0.2545)	4.19 (0.3090)	4.16 (0.3138)	4.17 (0.3129)

For the wavefunction methods, the difference between the values predicted with the 6-31+G(d) to 6-311+G(d) basis sets is minimal, and are within 0.10 eV of each other. The TD-DFT results show a similar trend, even for the largest aug-cc-pVTZ basis set. As such, it is clear that the effect of changing the basis set on the $\pi \rightarrow \pi^*$ electronic excitation is not significant. This is also supported by previous studies[1, 2], which suggests that for valence excited states, a double-ζ basis set with polarisation functions is already sufficient for the study of various classes of chromophores. Hence, we will use the 6-311+G(d) basis set for a compromise between computational cost and accuracy.

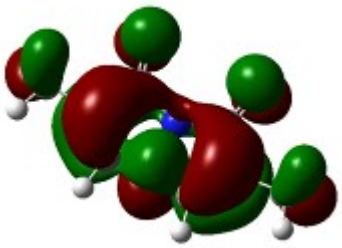
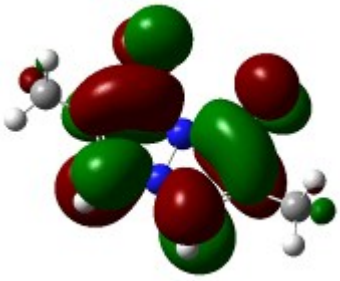
Vertical excitation energies of *syn*-bimanes

Table S2. The lowest three singlet excited states of the *syn*-bimane derivatives calculated with various correlated wavefunction methods and TD-DFT using different frequency-independent exchange-correlation kernels. The most expensive CR-EOM-CCSD(T) method was only carried out on **1**. All vertical excitation energies are in eV. Oscillator strengths for the electronic transitions are given in parentheses. The 6-311+G(d) basis set was used for all calculations.

		SAC-CI	EOM-CCSD [CR-EOM-CCSD(T)]	B3LYP	PBE0	M06	BMK	CAM-B3LYP	M06-2X
1	S_1	4.12 (0.3048)	4.06 (0.3118) [3.79]	3.77 (0.0000)	3.87 (0.0000)	3.94 (0.0000)	4.06 (0.2279)	4.16 (0.2266)	4.06 (0.2318)
	S_2	4.83 (0.0006)	4.46 (0.0000) [4.30]	3.85 (0.1954)	3.92 (0.2101)	3.96 (0.1966)	4.14 (0.0000)	4.30 (0.0000)	4.18 (0.0001)
	S_3	5.42 (0.0016)	5.09 (0.0000) [4.95]	4.41 (0.0027)	4.53 (0.0018)	4.60 (0.0024)	4.80 (0.0013)	4.92 (0.0001)	4.81 (0.0005)
2	S_1	3.79 (0.2691)	4.05 (0.3199)	3.71 (0.1974)	3.78 (0.2134)	3.81 (0.2037)	3.95 (0.2348)	4.07 (0.2357)	3.97 (0.2432)
	S_2	4.74 (0.0005)	4.54 (0.0000)	3.91 (0.0001)	4.01 (0.0001)	4.06 (0.0001)	4.25 (0.0001)	4.40 (0.0001)	4.27 (0.0001)
	S_3	5.23 (0.0087)	5.13 (0.0005)	4.54 (0.0075)	4.66 (0.0062)	4.53 (0.0006)	4.88 (0.0041)	5.00 (0.0031)	4.87 (0.0018)
3	S_1	3.58 (0.5468)	3.64 (0.6023)	3.17 (0.4024)	3.27 (0.4283)	3.23 (0.4226)	3.44 (0.4843)	3.49 (0.4946)	3.49 (0.5015)
	S_2	4.66 (0.0002)	4.41 (0.0001)	3.63 (0.0000)	3.75 (0.0000)	3.74 (0.0000)	4.05 (0.0000)	4.16 (0.0000)	4.12 (0.0000)
	S_3	5.49 (0.0027)	5.08 (0.0004)	4.45 (0.0211)	4.39 (0.0033)	4.37 (0.0025)	4.71 (0.0023)	4.80 (0.0021)	4.76 (0.0012)

4	S_1	3.93 (0.2646)	4.12	(0.2903)	3.81 (0.0000)	3.91 (0.0000)	3.99 (0.0001)	4.12 (0.2053)	4.22 (0.2085)	4.12 (0.2110)
	S_2	4.71 (0.0001)	4.49	(0.0000)	3.89 (0.1750)	3.97 (0.1881)	4.03 (0.1780)	4.18 (0.0001)	4.34 (0.0001)	4.22 (0.0001)
	S_3	5.29 (0.0042)	5.13	(0.0007)	4.46 (0.0045)	4.59 (0.0032)	4.66 (0.0048)	4.85 (0.0029)	4.98 (0.0028)	4.86 (0.0015)
5	S_1	3.99 (0.2017)	4.25	(0.2160)	3.81 (0.1103)	3.90 (0.1169)	3.88 (0.1135)	4.10 (0.1385)	4.12 (0.1454)	4.14 (0.1472)
	S_2	4.82 (0.0001)	4.64	(0.0001)	4.00 (0.0002)	4.12 (0.0002)	4.12 (0.0002)	4.34 (0.0002)	4.43 (0.0002)	4.35 (0.0002)
	S_3	5.41 (0.0235)	5.17	(0.0023)	4.62 (0.0155)	4.73 (0.0151)	4.73 (0.0141)	4.93 (0.0089)	4.99 (0.0090)	4.90 (0.0046)
6	S_1	3.73 (0.2740)	4.04	(0.3196)	3.60 (0.1761)	3.70 (0.1875)	3.65 (0.1844)	3.89 (0.2200)	3.94 (0.2306)	3.94 (0.2326)
	S_2	4.81 (0.0004)	4.60	(0.0001)	3.94 (0.0002)	4.05 (0.0002)	4.05 (0.0002)	4.31 (0.0002)	4.40 (0.0002)	4.33 (0.0002)
	S_3	5.34 (0.0121)	5.18	(0.0036)	4.56 (0.0158)	4.68 (0.0156)	4.68 (0.0015)	4.93 (0.0105)	4.99 (0.0106)	4.91 (0.0056)
7	S_1	3.78 (0.2464)	4.11	(0.2947)	3.75 (0.1705)	3.83 (0.1850)	3.87 (0.1782)	4.01 (0.2064)	4.12 (0.2114)	4.03 (0.2168)
	S_2	4.72 (0.0001)	4.57	(0.0001)	3.93 (0.0001)	4.04 (0.0001)	4.11 (0.0002)	4.28 (0.0001)	4.44 (0.0002)	4.30 (0.0001)
	S_3	5.01 (0.0091)	5.16	(0.0030)	4.57 (0.0124)	4.70 (0.0106)	4.43 (0.0015)	4.92 (0.0084)	5.04 (0.0076)	4.90 (0.0047)
8	S_1	3.58 (0.4898)	3.72	(0.5535)	3.25 (0.3533)	3.35 (0.3768)	3.33 (0.3726)	3.54 (0.4299)	3.60 (0.4436)	3.59 (0.4506)
	S_2	4.75 (0.0001)	4.47	(0.0000)	3.70 (0.0000)	3.82 (0.0000)	3.82 (0.0000)	4.13 (0.0000)	4.24 (0.0001)	4.19 (0.0000)
	S_3	5.34 (0.0011)	5.13	(0.0022)	4.33 (0.0068)	4.47 (0.0070)	4.47 (0.0002)	4.80 (0.0051)	4.88 (0.0059)	4.83 (0.0026)

Natural transition orbitals (NTOs) for the singlet excitation of the *syn*-bimanes

S_1	$\pi \rightarrow \pi^*$		

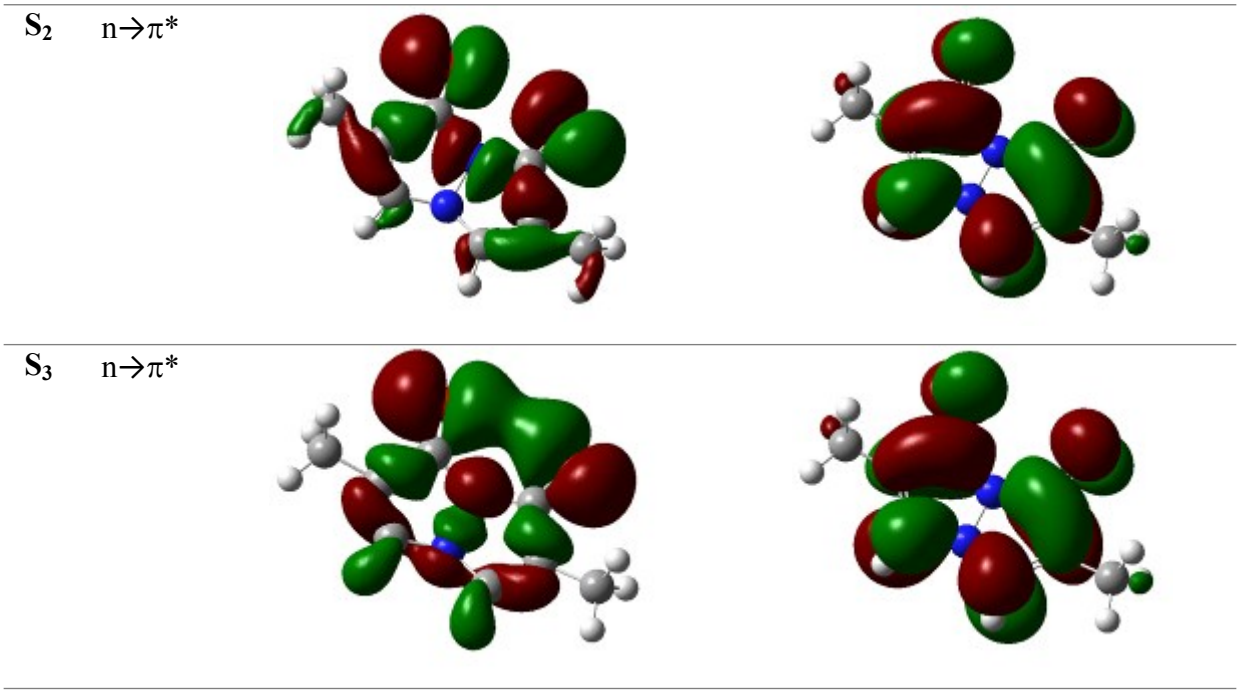


Figure S1. NTOs for the first three TD-B3LYP singlet excitations of **2**.

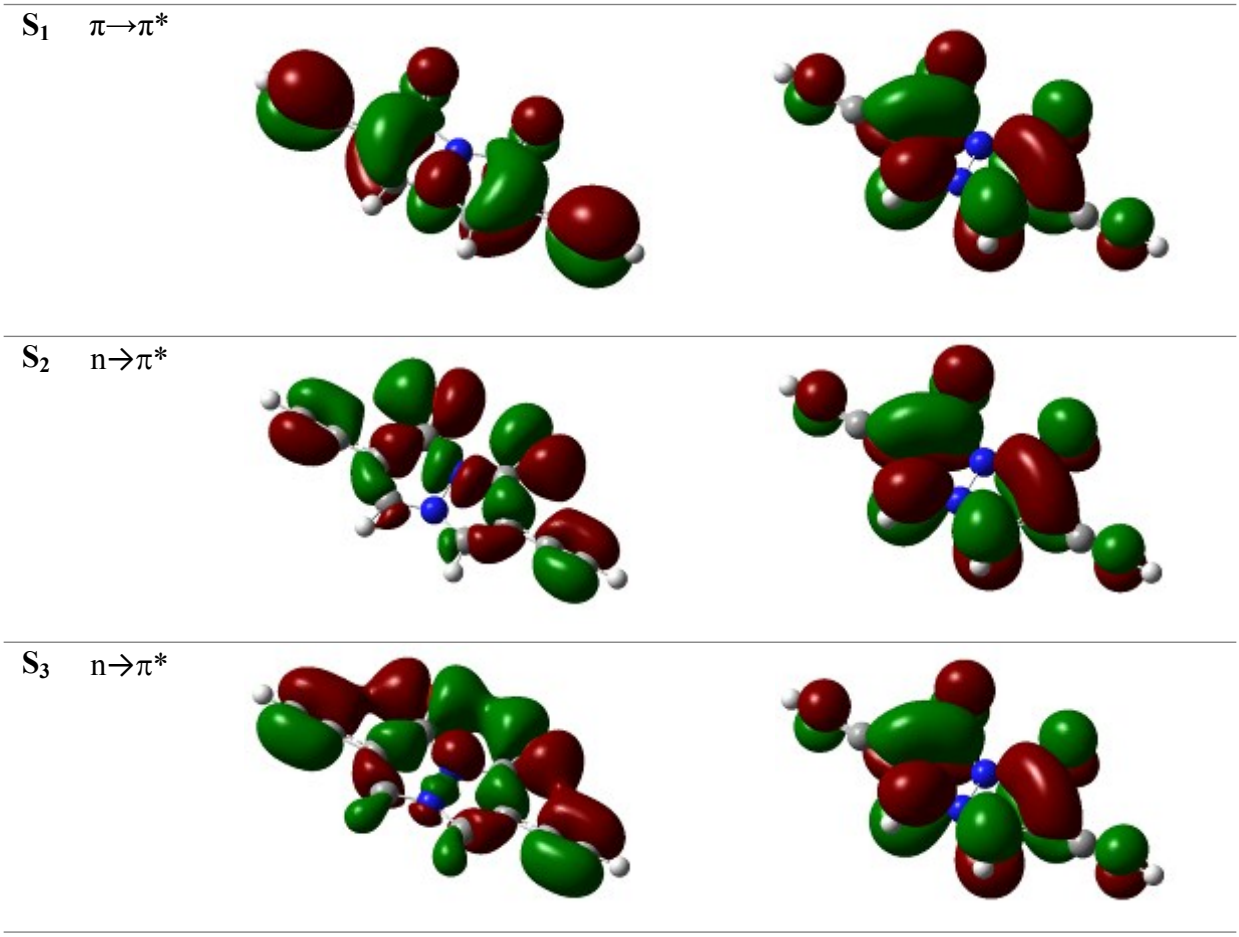


Figure S2. NTOs for the first three TD-B3LYP singlet excitations of **3**.

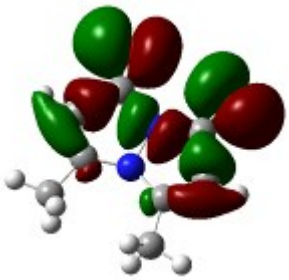
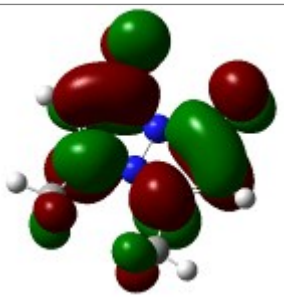
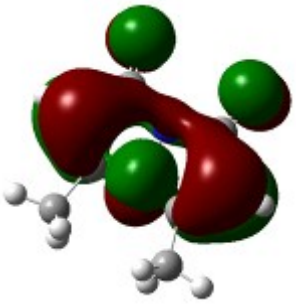
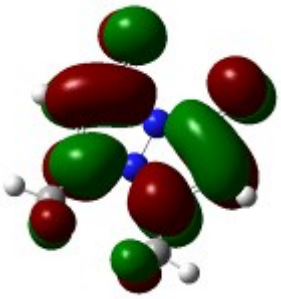
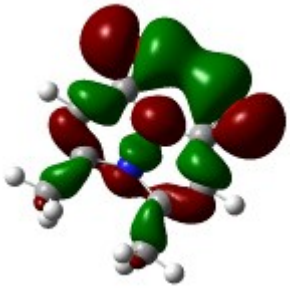
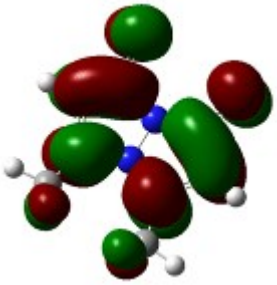
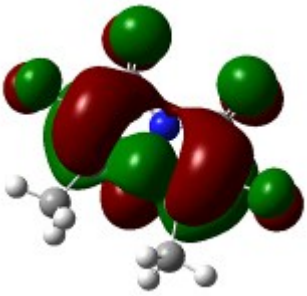
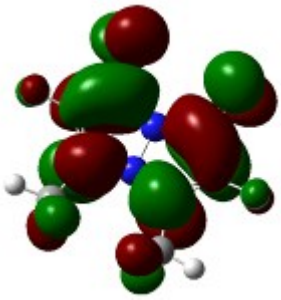
S_1	n→π*		
S_2	π→π*		
S_3	n→π*		

Figure S3. NTOs for the first three TD-B3LYP singlet excitations of **4**.

S_1	π→π*		

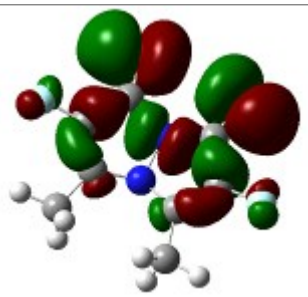
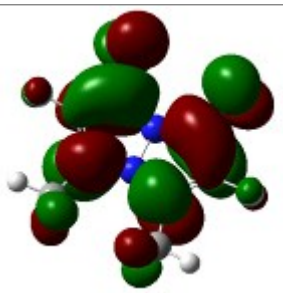
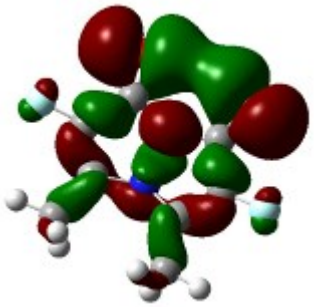
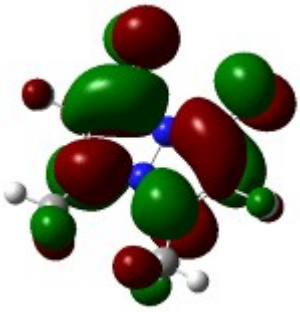
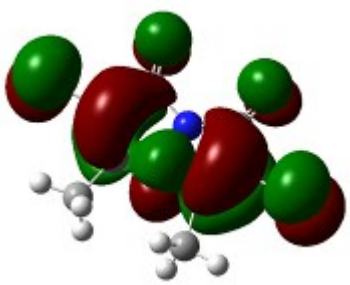
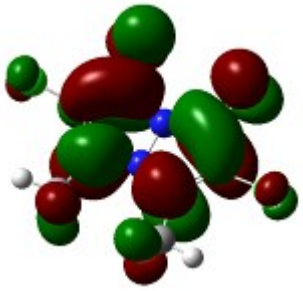
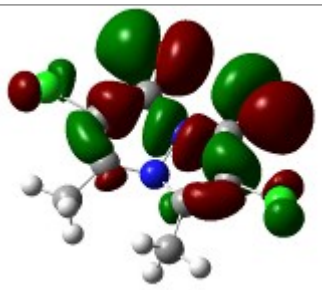
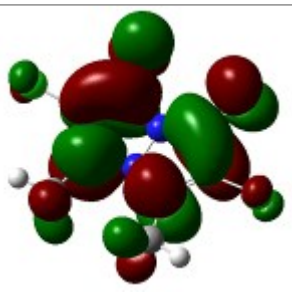
S_2	n→π*		
S_3	n→π*		

Figure S4. NTOs for the first three TD-B3LYP singlet excitations of **5**.

S_1	π→π*		
S_2	n→π*		

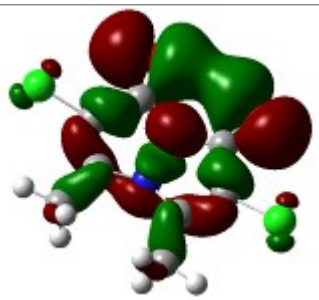
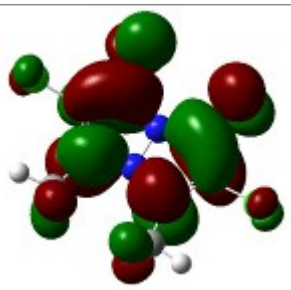
S_3	n→π*		

Figure S5. NTOs for the first three TD-B3LYP singlet excitations of **6**.

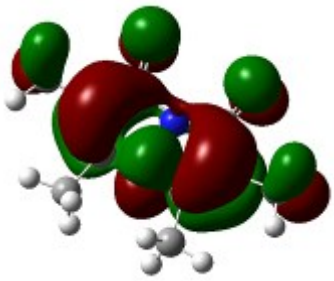
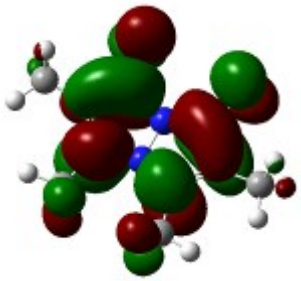
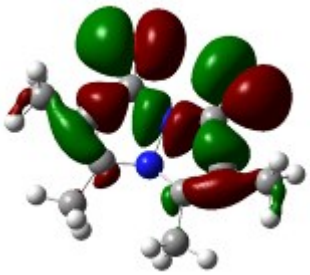
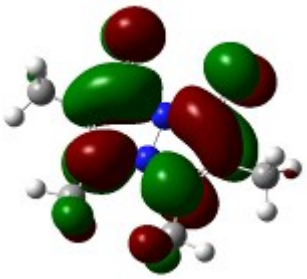
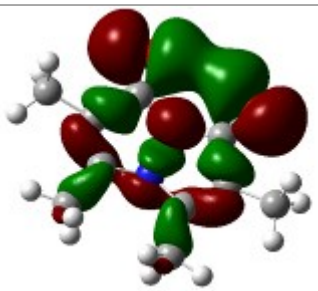
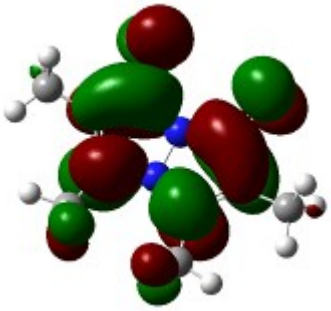
S_1	π→π*		
S_2	n→π*		
S_3	n→π*		

Figure S6. NTOs for the first three TD-B3LYP singlet excitations of **7**.

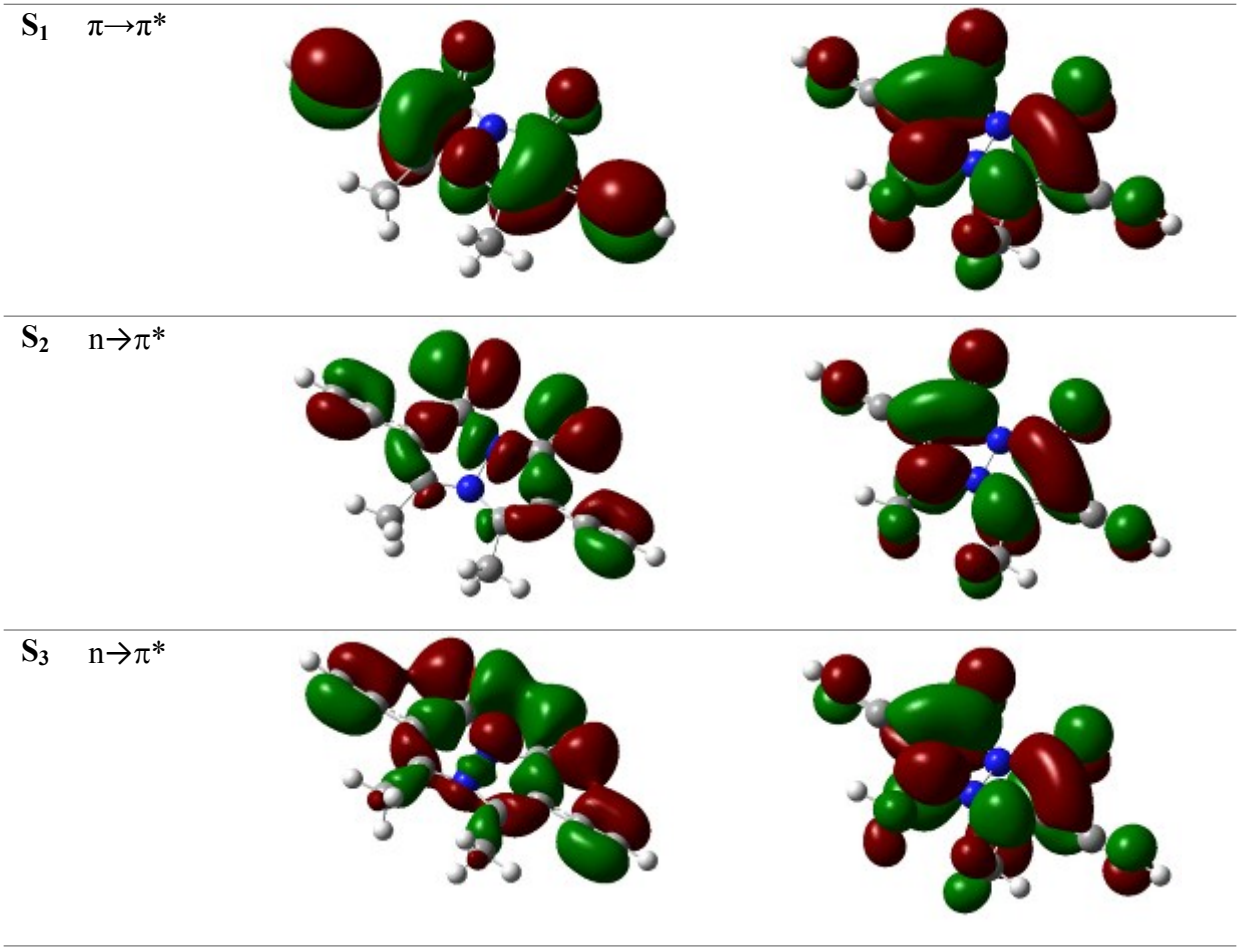


Figure S7. NTOs for the first three TD-B3LYP singlet excitations of **8**.

Solvation calculation results

Table S3. Experimental absorption and emission wavelengths for the *syn*-bimanes. All values are in eV.

Molecule	**Solvent**	λ_{abs}	λ_{emi}	**Ref.**
1	1,4-dioxane	3.41	3.17	[3]
	Acetonitrile	3.37	3.12	[4]
2	Acetonitrile	3.32	2.84	[4]
3	Acetonitrile	3.02	2.70	[5]

4	1,4-dioxane	3.50	3.20	[3]
5	1,4-dioxane	3.65	2.87	[3]
6	1,4-dioxane	3.37	2.89	[3]
7	1,4-dioxane	3.46	2.95	[3]
	Acetonitrile	3.37	2.85	[6]
	Ethanol	3.36	2.82	[7]
	Water	3.18	2.57	[8]
8	Acetonitrile	3.10	2.79	[9]

Table S4. Computational results for the *syn*-bimanes in solvent. ΔE^{vert} refers to the comparison done using the vertical transition energies, while λ refers to the comparison between the band maxima obtained from the vibrationally resolved absorption and emission spectra and the respective experimental values. All values are in eV.

	Solvent		**PCM**				**SMD**			
			ΔE_{abs}^{vert}	λ_{abs}	ΔE_{emi}^{vert}	λ_{emi}	ΔE_{abs}^{vert}	λ_{abs}	ΔE_{emi}^{vert}	λ_{emi}
1	1,4-dioxane	B3LYP	3.72	3.58	3.37	3.22	3.71	3.57	3.37	3.22
		PBE0	3.79	3.66	3.48	3.34	3.78	3.65	3.48	3.34
		M06	3.85	3.71	3.46	3.31	3.83	3.70	3.46	3.32
		BMK	3.97	3.86	3.56	3.43	3.96	3.85	3.57	3.44
		CAM-B3LYP	4.03	3.92	3.63	3.50	4.02	3.90	3.63	3.51
		M06-2X	4.08	3.96	3.62	3.48	4.05	3.93	3.62	3.49
1	Acetonitrile	B3LYP	3.51	3.41	3.05	2.94	3.53	3.43	3.05	2.94
		PBE0	3.58	3.49	3.18	3.07	3.60	3.51	3.18	3.08
		M06	3.67	3.57	3.18	3.07	3.68	3.58	3.18	3.07
		BMK	3.75	3.66	3.24	3.14	3.77	3.68	3.24	3.15
		CAM-B3LYP	3.82	3.73	3.33	3.23	3.83	3.74	3.33	3.23
		M06-2X	3.88	3.78	3.33	3.22	3.87	3.78	3.33	3.23
2	Acetonitrile	B3LYP	3.33	3.21	2.63	2.49	3.33	3.20	2.63	2.49
		PBE0	3.40	3.29	2.73	2.61	3.40	3.31	2.74	2.64
		M06	3.46	3.34	2.74	2.60	3.46	3.34	2.74	2.61
		BMK	3.61	3.50	2.82	2.71	3.61	3.50	2.83	2.72
		CAM-B3LYP	3.68	3.57	2.92	2.80	3.68	3.57	2.92	2.79

		M06-2X	3.75	3.63	2.92	2.79	3.75	3.63	2.92	2.80
3	Acetonitrile	B3LYP	2.94	2.84	2.41	2.31	3.04	2.94	2.51	2.41
		PBE0	3.07	2.98	2.56	2.46	3.17	3.08	2.66	2.57
		M06	3.11	3.01	2.60	2.49	3.21	3.11	2.70	2.60
		BMK	3.27	3.19	2.75	2.66	3.36	3.28	2.85	2.76
		CAM-B3LYP	3.39	3.30	2.90	2.80	3.47	3.38	2.99	2.90
		M06-2X	3.41	3.32	2.90	2.80	3.48	3.39	2.99	2.89
4	1,4-dioxane	B3LYP	3.76	3.61	3.37	3.21	3.76	3.62	3.37	3.22
		PBE0	3.84	3.70	3.48	3.34	3.85	3.71	3.49	3.34
		M06	3.93	3.79	3.48	3.33	3.91	3.77	3.49	3.34
		BMK	4.03	3.91	3.58	3.44	4.03	3.91	3.59	3.46
		CAM-B3LYP	4.09	3.97	3.66	3.53	4.08	3.96	3.67	3.54
		M06-2X	4.15	4.03	3.65	3.51	4.11	3.99	3.66	3.52
5	1,4-dioxane	B3LYP	3.66	3.52	2.86	2.71	3.67	3.53	2.87	2.73
		PBE0	3.75	3.62	2.94	2.80	3.75	3.62	2.96	2.83
		M06	3.81	3.68	2.97	2.83	3.82	3.69	2.99	2.85
		BMK	3.99	3.88	3.06	2.93	3.99	3.87	3.08	2.96
		CAM-B3LYP	4.03	3.91	3.17	3.04	4.04	3.92	3.19	3.06
		M06-2X	4.15	4.02	3.16	3.03	4.14	4.02	3.18	3.05
6	1,4-dioxane	B3LYP	3.45	3.34	2.84	2.72	3.46	3.35	2.89	2.77
		PBE0	3.53	3.43	2.93	2.82	3.54	3.43	2.99	2.87
		M06	3.58	3.48	2.92	2.81	3.58	3.47	2.98	2.86
		BMK	3.80	3.70	3.11	3.00	3.79	3.70	3.16	3.07
		CAM-B3LYP	3.86	3.77	3.20	3.10	3.86	3.76	3.25	3.14
		M06-2X	3.95	3.84	3.18	3.06	3.94	3.84	3.22	3.11
7	1,4-dioxane	B3LYP	3.58	3.45	2.95	2.81	3.55	3.41	2.97	2.81
		PBE0	3.66	3.54	3.05	2.92	3.63	3.50	3.06	2.91
		M06	3.73	3.58	3.04	2.89	3.69	3.55	3.05	2.90
		BMK	3.88	3.76	3.17	3.05	3.83	3.70	3.18	3.04
		CAM-B3LYP	3.95	3.84	3.25	3.13	3.91	3.79	3.27	3.14
		M06-2X	4.03	3.89	3.24	3.08	3.99	3.85	3.25	3.10
7	Acetonitrile	B3LYP	3.35	3.24	2.62	2.50	3.35	3.22	2.62	2.49
		PBE0	3.43	3.33	2.72	2.61	3.44	3.32	2.73	2.60
		M06	3.51	3.39	2.74	2.61	3.51	3.38	2.77	2.63
		BMK	3.61	3.51	2.81	2.71	3.61	3.51	2.88	2.76
		CAM-B3LYP	3.70	3.61	2.91	2.81	3.69	3.58	2.92	2.80

		M06-2X	3.80	3.68	2.90	2.76	3.79	3.67	2.92	2.79
7	Ethanol	B3LYP	3.36	3.25	2.63	2.51	3.20	3.08	2.41	2.29
		PBE0	3.44	3.34	2.74	2.63	3.28	3.17	2.50	2.37
		M06	3.52	3.40	2.75	2.62	3.36	3.26	2.55	2.43
		BMK	3.62	3.52	2.83	2.72	3.47	3.37	2.60	2.49
		CAM-B3LYP	3.71	3.62	2.93	2.83	3.55	3.45	2.72	2.61
		M06-2X	3.81	3.69	2.92	2.79	3.65	3.54	2.68	2.56
7	Water	B3LYP	3.34	3.23	2.60	2.48	3.21	3.10	2.32	2.20
		PBE0	3.42	3.32	2.70	2.60	3.31	3.20	2.41	2.29
		M06	3.50	3.38	2.73	2.60	3.39	3.29	2.44	2.32
		BMK	3.60	3.50	2.80	2.69	3.50	3.40	2.49	2.38
		CAM-B3LYP	3.69	3.60	2.89	2.80	3.58	3.49	2.60	2.50
		M06-2X	3.79	3.67	2.88	2.75	3.68	3.57	2.56	2.44
6	Acetonitrile	B3LYP	2.99	2.90	2.46	2.36	3.11	3.01	2.57	2.47
		PBE0	3.13	3.04	2.61	2.51	3.25	3.16	2.73	2.62
		M06	3.21	3.11	2.66	2.55	3.31	3.21	2.77	2.66
		BMK	3.36	3.28	2.81	2.72	3.45	3.37	2.93	2.84
		CAM-B3LYP	3.47	3.39	2.96	2.87	3.57	3.49	3.07	2.98
		M06-2X	3.50	3.41	2.95	2.85	3.60	3.51	3.05	2.96

Statistical results with SMD model

Table S5. Mean signed and unsigned absolute errors (MSE and MUE), and standard deviation (SD) obtained by comparing computational and experimental values. ΔE^{vert} refers to the comparison done using the vertical transition energies, while λ refers to the comparison between the band maxima obtained from the vibrationally resolved absorption and emission spectra and the respective experimental values. All values are in eV.

	Absorption					
	MSE		MUE		SD	
	ΔE_{abs}^{vert}	λ_{abs}	ΔE_{abs}^{vert}	λ_{abs}	ΔE_{abs}^{vert}	λ_{abs}
B3LYP	0.067	-0.053	0.098	0.109	0.099	0.065
PBE0	0.158	0.047	0.171	0.093	0.106	0.077
M06	0.221	0.104	0.221	0.122	0.182	0.087

BMK	0.355	0.253	0.355	0.253	0.156	0.112
CAM-B3LYP	0.431	0.329	0.431	0.329	0.211	0.106
M06-2X	0.495	0.386	0.495	0.386	0.222	0.088

Emission						
	MSE		MUE		SD	
	ΔE_{emi}^{vert}	λ_{emi}	ΔE_{emi}^{vert}	λ_{emi}	ΔE_{emi}^{vert}	λ_{emi}
B3LYP	-0.097	-0.227	0.164	0.238	0.116	0.147
PBE0	0.014	-0.106	0.147	0.159	0.098	0.120
M06	0.028	-0.098	0.130	0.146	0.121	0.107
BMK	0.137	0.026	0.189	0.149	0.125	0.093
CAM-B3LYP	0.233	0.119	0.249	0.182	0.183	0.093
M06-2X	0.218	0.100	0.243	0.0182	0.182	0.086

Calculation of fluorescence lifetimes with TD-DFT

Table S6. Experimental quantum yields (ϕ_f) and fluorescence lifetimes (τ_f) of the *syn*-bimanes. *Quantum yield taken to be 1.00 for **7**. All lifetime values are in ns.

Molecule	**Solvent**	ϕ_f	τ_f	**Ref.**
1	1,4-dioxane	0.92	7.4	[3]
4	1,4-dioxane	0.97	9.8	[3]
5	1,4-dioxane	1.00	17.0	[3]
6	1,4-dioxane	1.02*	10.7	[3]
7	1,4-dioxane	0.90	12.3	[3]

Table S7. Computational fluorescence lifetime results for *syn*-bimanes in 1,4-dioxane. All values are in ns.

PCM						
	B3LYP	PBE0	M06	BMK	CAM-B3LYP	M06-2X
1	8.8	7.2	7.9	5.7	5.7	5.1

4	12.2	10.1	9.4	7.7	7.1	6.4
5	26.8	22.9	22.3	18.1	15.1	13.8
6	14.4	12.4	12.0	9.9	8.0	8.1
7	12.7	10.7	10.8	8.5	7.7	8.0

				SMD		
	B3LYP	PBE0	M06	BMK	CAM-B3LYP	M06-2X
1	8.6	7.1	7.8	5.6	5.6	5.0
4	12.1	10.0	9.2	7.3	7.3	6.3
5	27.1	21.7	21.9	16.9	14.4	14.2
6	13.3	11.2	11.5	8.3	7.4	7.5
7	13.5	10.8	10.9	8.7	8.0	8.0

Table S8. The mean signed (MSE) and percentage error (MPE) for fluorescence lifetimes calculated using the SMD model. The MSE is reported in ns, and the MPE is a percentage.

	MSE	**MUE**	**MPE**
B3LYP	3.5	3.5	26.9
PBE0	0.7	1.4	10.0
M06	0.8	1.6	11.8
BMK	-2.1	2.1	20.4
CAM-B3LYP	-2.9	2.9	25.9
M06-2X	-3.2	3.2	30.0

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