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Supplementary Material

Using new solvatochromic parameters to investigate dye–solvent interactions

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SUPPLEMENTARY INFORMATION

Using New Solvatochromic Parameters to Investigate Dye-Solvent Interactions

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Contents

S1. Gaussian 16 reference

Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

S2. Spectroscopic data obtained from semi-empirical methods and experimental values

The ground state absorption maxima (λ_{grd}^{calc}) and oscillator strength (*f*) have been calculated using ZINDO/S for vertical excitation energies of 2-methylthio-3-methyluracil (**2MT-3MU**) and triazine dyes **1** to **7** optimised using the AM1, PM3 and PM6 methods. Experimental data for triazine dyes **1** to **7** were either obtained from ref. [41] or measured directly, while **2MT-3MU** experimental data was obtained from ref. [37]. Computational data for dyes **1** to **7** were obtained from ref. [26]. ND, not determined.

Table S1. Comparative data obtained from semi-empirical methods and experimental values.

Dye	Medium	λ_{grd}^{exp}	AM1		PM3		PM6	
			λ_{grd}^{calc}	*f*	λ_{grd}^{calc}	*f*	λ_{grd}^{calc}	*f*
2MT-3MU	Vacuum	290	302	0.241	296	0.240	301	0.237
BPT **1**	Vacuum	ND	401	0.265	374	0.090	388	0.243
	DMSO	385	420	0.277	386	0.169	412	0.309
	THF	381	418	0.279	385	0.180	409	0.288
	MeCN	380	420	0.239	391	0.144	410	0.301
	2-MeTHF	381	420	0.259	385[A]	0.180[A]	411	0.260
	Toluene	385	416	0.282	386	0.192	408	0.199
MPT **2**	Vacuum	ND	401	0.249	374	0.080	387	0.229
	DMSO	387	429	0.315	384[A]	0.167[A]	411	0.291
	THF	384	418	0.259	394	0.177	408	0.271
	MeCN	389	419	0.254	382	0.162	410	0.284
	2-MeTHF	384	418	0.259	394	0.177	408	0.270
	Toluene	387	422	0.280	392	0.170	407	0.224
BDT **3**	Vacuum	ND	400[A]	0.257[A]	376	0.128	389	0.251
	DMSO	382	422[A]	0.270[A]	387	0.169	413	0.327
	THF	379	420	0.285	384	0.176	411	0.314
	MeCN	378	420[A]	0.267[A]	386	0.166	411	0.307
	2-MeTHF	378	420	0.285	384	0.177	411[A]	0.313[A]
	Toluene	384	420	0.301	385	0.195	410	0.245
MOT **4**	Vacuum	ND	389	0.272	364	0.150	373	0.213
	DMSO	388	420	0.324	387	0.181	402	0.244
	THF	381	416	0.320	383[A]	0.168[A]	399	0.271
	MeCN	381	417	0.319	386	0.178	401	0.240
	DMF	389	420	0.325	387	0.183	402	0.245
AMT **5**	Vacuum	ND	395	0.257	373	0.103	383	0.253
	DMSO	401	423[A]	0.312[A]	394	0.168	410[A]	0.301[A]
	THF	393	419	0.307	386	0.154	406	0.304
	MeCN	393	420	0.307	393	0.163	408[A]	0.295[A]
	DMF	404	423	0.313	394	0.167	411[A]	0.302[A]

BMT **6**	Vacuum	ND	395	0.220	375	0.082	383	0.175
	DMSO	406	424	0.264	395	0.167	410	0.234
	THF	397	421	0.262	391	0.169	410	0.223
	MeCN	396	423	0.260	394	0.164	408	0.228
	DMF	409	424	0.265	395	0.168	410	0.234
EOT **7**	Vacuum	ND	397	0.254	379	0.130	387	0.263
	DMSO	399	419	0.260	385	0.167	407	0.288
	THF	393	417	0.268	384	0.182	408	0.307
	MeCN	395	417	0.256	384	0.164	405	0.283
	DMF	397	419	0.261	386	0.169	407	0.289

[A]Structure optimised based on negligible forces.

S3. Comparative electronic ground state absorption (λ_{grd}^{calc}) and excited state emission (λ_{exc}^{calc}) data with the corresponding oscillator strengths (*f*) for EOT (7)

Comparison of the ground state absorption maxima (λ_{grd}^{calc}), excited state emission (λ_{exc}^{calc}) data and associated oscillator strengths (*f*) were calculated using TDDFT analysis at the ωB97X-D/6-31G(d) level for 2-methylthio-3-methyluracil (**2MT-3MU**) and triazine dye **EOT**. Experimental data for **EOT** was either obtained from ref. [41] or measured directly, while **2MT-3MU** experimental data was obtained from ref. [37]. Computational data for dyes **EOT** was obtained from ref. [26]. λ_{grd}^{exp} and λ_{exc}^{exp} are the experimental absorption and emission maxima respectively. Computational absorptions were calculated using (i) the linear response or (ii) state-specific solvation models. The emission data were calculated only through the state-specific approach. ND, not determined.

Table S2. Comparative data obtained for **EOT (7)** and **2MT-3MU** using TDDFT calculations.

		EOT (7)			**2MT-3MU**		
Calculation	Medium	λ_{grd}^{exp} [nm]	λ_{grd}^{calc} [nm]	*f*	λ_{grd}^{exp} [nm]	λ_{grd}^{calc} [nm]	*f*
TDDFT, obtained from vertical excitation energies, linear response solvation	Vacuum[A]	ND	396	0.166	290	253	0.202
	DMSO	399	405	0.213	-	-	-
	THF	393	405	0.211	-	-	-
TDDFT, obtained from vertical excitation energies, state-specific solvation	DMSO	399	401	0.168	-	-	-
	THF	393	401	0.167	-	-	-
		λ_{exc}^{exp} [nm]	λ_{exc}^{calc} [nm]	*f*	λ_{exc}^{exp} [nm]	λ_{exc}^{calc} [nm]	*f*
TDDFT, obtained from adiabatic excitation energies, state-specific solvation	Vacuum[A]	ND	501	0.125	-	300	0.172
	DMSO	527	517	0.125	-	-	-
	THF	496	514	0.125	-	-	-

[A]Calculations completed under vacuum involve no implicit solvation model.