Electronic Supplementary Information (ESI)

Novel formazan derivatives containing phenylsulfanyl and carbonyl units: Synthesis, optical and electrochemical properties

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Table S1 UV-Vis	. absorption λ _{max}	values of formazans	(4a–4h) ii	n various so	lvents
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Comp.	DMSO	DMF	EtOH	MeOH	Acetone	1,4-Dioxane	EtOAc
4a	517	515	517	505	504	512	509
	304	302	304	298		302	302
4b	521	512	499	490	498	501	499
	368, 311	361, 310	285	285	363	310	355
4c	537	531	522	521	521	525	522
	304	304	302	302		303	302
4d	537	531	526	527	526	527	526
	306	303	303	415, 304		303	305
4e	521	513	501	506	505	506	507
	303	302	300	301		302	301
4f	501	515	523	524	521	530	523
	378	374	364, 295	514, 362	364	364, 297	364, 295
4g	515	510	498	499	504	502	503
Ū	308	309	304	305		306	304
4h	409	503	390	389	489	483	484
		260	204	200	265	262	365
		509	294	209	505	505	505
Comp.	2-Propanol	CHCl ₃	THF	1-Butanol	Toluene	Cyclohexane	n-Hexane
Comp. 4a	2-Propanol 507	CHCl₃ 510	THF 511	1-Butanol 513	Toluene 524	Cyclohexane 507	n-Hexane 511
Comp. 4a	2-Propanol 507 299	CHCl₃ 510 303	THF 511 302	1-Butanol 513 303	Toluene 524 304	Cyclohexane 507 405, 301	n-Hexane 511 403
Comp. 4a 4b	2-Propanol 507 299 499	CHCl₃ 510 303 502	THF 511 302 507	1-Butanol 513 303 497	Toluene 524 304 515	505 Cyclohexane 507 405, 301 495	n-Hexane 511 403 490
Comp. 4a 4b	2-Propanol 507 299 499 285	CHCl₃ 510 303 502 309	THF 511 302 507 362	1-Butanol 513 303 497 286	Toluene 524 304 515 357	Sos Cyclohexane 507 405, 301 495 325, 310	n-Hexane 511 403 490 361
Comp. 4a 4b 4c	2-Propanol 507 299 499 285 522	CHCl ₃ 510 303 502 309 531	THF 511 302 507 362 531	1-Butanol 513 303 497 286 528	Toluene 524 304 515 357 532	Sos Cyclohexane 507 405, 301 495 325, 310 526	n-Hexane 511 403 490 361 520
Comp. 4a 4b 4c	2-Propanol 507 299 499 285 522 303	S09 CHCl₃ 510 303 502 309 531 307	Z94 THF 511 302 507 362 531 303	1-Butanol 513 303 497 286 528 302	Toluene 524 304 515 357 532 306	Sos Cyclohexane 507 405, 301 495 325, 310 526 304	n-Hexane 511 403 490 361 520 414
Comp. 4a 4b 4c 4d	2-Propanol 507 299 499 285 522 303 531	CHCl ₃ 510 303 502 309 531 307 530	Z94 THF 511 302 507 362 531 303 535	1-Butanol 513 303 497 286 528 302 523	Toluene 524 304 515 357 532 306 536	Sos Cyclohexane 507 405, 301 495 325, 310 526 304 531	n-Hexane 511 403 490 361 520 414 527
Comp. 4a 4b 4c 4d	2-Propanol 507 299 499 285 522 303 531 303	CHCl ₃ 510 303 502 309 531 307 530 306	Z94 THF 511 302 507 362 531 303 535 305	1-Butanol 513 303 497 286 528 302 523 303	Toluene 524 304 515 357 532 306 536 305	S03 Cyclohexane 507 405, 301 495 325, 310 526 304 531 419	n-Hexane 511 403 490 361 520 414 527 415
Comp. 4a 4b 4c 4d 4d	2-Propanol 507 299 499 285 522 303 531 303 508	S09 CHCl₃ 510 303 502 309 531 307 530 306 509	Z94 THF 511 302 507 362 531 303 535 305 514	233 1-Butanol 513 303 497 286 528 302 523 303 512	Toluene 524 304 515 357 532 306 536 305 514	S03 Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511	n-Hexane 511 403 490 361 520 414 527 415 508
Comp. 4a 4b 4c 4d 4e	2-Propanol 507 299 499 285 522 303 531 303 531 303 508 302	CHCl ₃ 510 303 502 309 531 307 530 306 509 301	Z94 THF 511 302 507 362 531 303 535 305 514 304	283 1-Butanol 513 303 497 286 528 302 523 303 512 301	Toluene 524 304 515 357 532 306 536 305 514 305	Sos Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511 300	n-Hexane 511 403 490 361 520 414 527 415 508 406
Comp. 4a 4b 4c 4d 4d 4e 4f	2-Propanol 507 299 499 285 522 303 531 303 531 303 508 302 522	CHCl ₃ 510 303 502 309 531 307 530 306 509 301 523	Z94 THF 511 302 507 362 531 303 535 305 514 304 530	1-Butanol 513 303 497 286 528 302 523 303 512 301 528	Toluene 524 304 515 357 532 306 536 305 514 305 537	S03 Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511 300 446	n-Hexane 511 403 490 361 520 414 527 415 508 406 442
Comp. 4a 4b 4c 4d 4e 4f	2-Propanol 507 299 499 285 522 303 531 303 531 303 508 302 508 302 522 361, 302	CHCl ₃ 510 303 502 309 531 307 530 306 509 301 523 374	Z94 THF 511 302 507 362 531 303 535 305 514 304 530 366, 300	283 1-Butanol 513 303 497 286 528 302 523 303 512 301 528 301 528 364, 386	Toluene 524 304 515 357 532 306 536 305 514 305 537 366	Sos Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511 300 446 274	n-Hexane 511 403 490 361 520 414 527 415 508 406 442 361, 286
Comp. 4a 4b 4c 4d 4d 4e 4f 4g	2-Propanol 507 299 499 285 522 303 531 303 531 303 508 302 508 302 522 361, 302 502	CHCl ₃ 510 303 502 309 531 307 530 306 509 301 523 374 503	Z94 THF 511 302 507 362 531 303 535 305 514 304 530 366, 300 508	283 1-Butanol 513 303 497 286 528 302 523 303 512 301 528 364, 386 505	Toluene 524 304 515 357 532 306 536 305 514 305 537 366 509	S03 Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511 300 446 274 499	n-Hexane 511 403 490 361 520 414 527 415 508 406 442 361, 286 498
Comp. 4a 4b 4c 4d 4d 4e 4f 4g	2-Propanol 507 299 499 285 522 303 531 303 531 303 508 302 522 361, 302 502 361, 302	CHCl ₃ 510 303 502 309 531 307 530 306 509 301 523 374 503 309	Z94 THF 511 302 507 362 531 303 535 305 514 304 530 366, 300 508 308	283 1-Butanol 513 303 497 286 528 302 523 303 512 301 528 364, 386 505 307	Toluene 524 304 515 357 532 306 536 305 514 305 537 366 509 309	S03 Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511 300 446 274 499 405	n-Hexane 511 403 490 361 520 414 527 415 508 406 442 361, 286 498 354
Comp. 4a 4b 4c 4d 4c 4d 4e 4f 4g 4h	2-Propanol 507 299 499 285 522 303 531 303 508 302 508 302 522 361, 302 502 304 386	CHCl ₃ 510 303 502 309 531 307 530 306 509 301 523 374 503 309 496	294 THF 511 302 507 362 531 303 535 305 514 304 530 366, 300 508 308 494	283 1-Butanol 513 303 497 286 528 302 523 303 512 301 528 364, 386 505 307 385	S03 Toluene 524 304 515 357 532 306 536 305 514 305 537 366 509 309 503	Sos Cyclohexane 507 405, 301 495 325, 310 526 304 531 419 511 300 446 274 499 405	n-Hexane 511 403 490 361 520 414 527 415 508 406 442 361, 286 498 354 478

Comp.	DMSO	DMF	EtOH	MeOH	Acetone	Dioxane	EtOAc
5a	505 307	507 305	501 303	498 303	502	501 305	503 304
5b	513 372, 313	506 368, 313	503 364, 309	500 365, 310	502 365	502 365, 310	500 299, 272
5c	520 313	517 309	512 307	511 307	515	512 307	515 309
5d	524 311	520 310	517 307	512 308	526 364	517 308	516 310
5e	508 307	507 306	501 306	499 305	503	502 305	500 306
5f	496	494	533 377, 299	530 394, 289	525 372	540 368, 304	537 371, 304
5g	506 311	506 310	499 309	500 306	498 359	500 311	500 308
5h	406	402	388	391	391	386	386
Comp.	Propanol	CHCl₃	THF	1-Butanol	Toluene	Cyclohexane	n-Hexane
5a	500 300	503 308	506 306	503 303	509 417, 306	505 304	504 302
5b	503 365, 311	496 364, 314	506 368, 313	504 366, 310	512 367, 312	506 361, 312	502 361, 312
5c	511 308	509 311	520 310	513 309	518 311	516 412, 309	516 461, 307
5d	531 303	515 312	517 310	519 309	523 313	518 417, 310	517 311
5e	502 303	498 309	504 308	503 305	511 311	506 303	503 426, 306
5f	534 376, 310	548 372, 304	539 371	538 372, 303	552 367, 306	549 360, 307	568 363
5g	498 309	499 312	506 311	501 307	503 311	503 308	502 310
5h	390 303	389	391	389	388	379	369

Table S2 UV-vis absorption λ_{max} values of formazans (5a–5h) in different solvents

Table S3. Calculated sum of electronic and thermal free energies (SETFE) (in Hatree) of compounds 4a-4h and 5a-5h andsome important bond distances of tautomer forms predicted at PBE1PBE/6-311g(2d,2p) level (in Å) in gasphase.

				H–bond (Å)						
Comp.	SI	SETFE		Tautomeric form 1			Tautomeric form 2			
	Tautomer 1	Tautomer 2	$\Delta_{\rm KT}{}^{\rm a}$	H1…N2	H1…S1	H1…O1	H2…N1	H2…S1	H2…O1	
4a	-1694.6068	-1694.6026	0.004	1.788	3.051	-	1.840	2.670		
4b	-1809.0035	-1809.0067	-0.003	1.772	3.045	-	1.842	2.671		
4c	-2154.0435	-2154.0459	-0.002	1.683	2.931	-	1.835	2.664		
4d	-4267.7524	-4267.7536	-0.001	1.784	3.042	-	1.837	2.665		
4e	-1793.7951	-1793.7945	0.001	1.782	3.045	-	1.840	2.666		
4f	-1898.9917	-1898.9912	0.001	1.804	3.038	-	1.825	2.662		
4g	-1773.0942	-1773.1009	-0.007	1.783	3.055	-	1.732	2.668		
4h	-2103.3694	-2103.3611	0.008	1.940	3.543	1.928	1.789	4.321	2.135	
5a	-1869.251	-1869.246	0.005	1.850	-	2.313	1.799	-	3.480	
5b	-1983.646	-1983.648	-0.002	1.832	-	2.297	1.807	-	3.491	
5c	-2328.690	-2328.688	0.002	1.852	-	2.273	1.789	-	3.367	
5d	-4442.355	-4442.396	-0.041	1.855	-	2.365	1.795	-	3.398	
5e	-1968.437	-1968.437	0.000	1.749	-	2.139	1.791	-	3.352	
5f	-2073.629	-2073.637	-0.008	1.783	-	2.132	1.917	-	1.982	
5g	-1949.383	-1947.647	1.736	1.845	-	2.298	1.796	-	3.459	
5h	-2278.007	-2278.010	-0.002	1.885	-	2.221	1.899	-	1.972	

^a Δ_{KT} = E_{tautomer form2} - E_{tautomer form1}, Δ_{KT} constant stable between tautomer forms.



S5



S6



Figure S1 HOMO and LUMO electronic density distributions of 4a-4h calculated at PBE1PBE/6-311g (2d,2p) level



Comp.

HOMO (eV)

LUMO (eV)







Figure S2 HOMO and LUMO electronic density distributions of 5a–5h calculated at PBE1PBE/6-311g (2d,2p) level

NMR spectra of target compounds



Figure S3 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, DMSO-d⁶) spectra of compound 4a



Figure S4 a) ¹H NMR (500 MHz, CDCl₃), b) ¹³C NMR (126 MHz, CDCl₃) spectra of compound 4b



Figure S5 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, DMSO-d₆) spectra of compound 4c



Figure S6 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, CDCl₃) spectra of compound 4d



Figure S7 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, DMSO-d₆) spectra of compound 4e



Figure S8 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, DMSO-d₆) spectra of compound 4f



Figure S9 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, DMSO-d₆) spectra of compound 4g



Figure S10 a) 1 H NMR (500 MHz, DMSO-d₆), b) 13 C NMR (126 MHz, CDCl₃) spectra of compound 4h



Figure S11 a) ¹H NMR (500 MHz, CDCl₃), b) ¹³C NMR (126 MHz, CDCl₃) spectra of compound 5a



Figure S12 a) 1 H NMR (500 MHz, DMSO-d₆), b) 13 C NMR (126 MHz, CDCl₃) spectra of compound 5b







Figure S14 a) 1 H NMR (500 MHz, CDCl₃), b) 13 C NMR (126 MHz, CDCl₃) spectra of compound 5d



Figure S15 a) 1 H NMR (500 MHz, CDCl₃), b) 13 C NMR (126 MHz, CDCl₃) spectra of compound 5e







Figure S17 a) ¹H NMR (500 MHz, DMSO-d₆), b) ¹³C NMR (126 MHz, CDCl₃) spectra of compound 5g



Figure S18 a) 1 H NMR (500 MHz, DMSO-d₆), b) 13 C NMR (126 MHz, DMSO-d₆) spectra of compound 5h