Tuning the photophysical properties of 4′-subsituted terpyridines - experimental and theoretical study

ELECTRONIC SUPLEMENTARY INFORMATION

Anna Maroń[a], Agata Szlapa[b], Tomasz Klemens[a], Slawomir Kula[b], Barbara Machura[a]*, Stanisław Krompiec[b], Jan Grzegorz Małecki[a], Anna Świtlicka-Olszewska[a], Karol Erfurt[c], Anna Chrobok[c]

[a]*Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland*

[b]*Department of Inorganic, Organometallic Chemistry and Catalysis, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland*

[c]*Department of Chemical Organic Technology and Petrochemistry, Silesian University of Technology, Krzywoustego 4, 44-100 Gliwice, Poland*

Abstract: Several 2,2′:6′,2″-terpyridines substituted in 4′-position were synthetized and their photophysical properties were investigated by absorption and photoluminescence spectroscopy in dilute solutions and solid state. The studies confirmed that the absorption and emission wavelengths, fluorescence quantum yields and lifetimes of **1-R[1-16]** are strongly structure-related, demonstrating a decisive role of the nature of the substituent in determining photophysical properties of 4′-functionalized terpyridines. Additionally, the density functional theory (DFT) calculations were performed for **1-R[1-16]** to get an insight into their electronic structure and spectroscopic properties.

Keywords: 2,2′:6′,2″-terpyridine derivatives, absorption and fluorescence spectra, effect of solvent polarity, intramolecular charge transfer, DFT calculations.

* Corresponding author, email: bmachura@poczta.onet.pl

Tables:

Figures:

Table S1. Experimental and calculated bond lengths [Å] and angles [°] for 2.2′:6′.2″-terpyridine derivatives.

Bonds [Å]					Angles [°]				
1-R³									
exp				calc	exp				calc
N(1)–C(1)	1.340(2)	N(4)–C(27)	1.339(2)	1.353	C(1)–N(1)–C(5)	122.74(17)	C(27)–N(4)–C(31)	117.57(15)	118.74
N(1)–C(5)	1.345(2)	N(4)–C(31)	1.347(2)	1.354	C(10)–N(2)–C(6)	116.50(15)	C(32)–N(5)–C(36)	116.8(2)	118.74
N(2)–C(6)	1.337(2)	N(5)–C(32)	1.339(3)	1.358	C(15)–N(3)–C(11)	116.8(2)	C(41)–N(6)–C(37)	116.69(18)	118.76
N(2)–C(10)	1.342(3)	N(5)–C(36)	1.345(3)	1.347	N(1)–C(1)–C(2)	122.74(17)	N(4)–C(27)–C(28)	122.94(16)	122.10
N(3)–C(11)	1.345(3)	N(6)–C(37)	1.344(2)	1.358	N(1)–C(1)–C(6)	116.50(15)	N(4)–C(27)–C(32)	116.31(15)	117.11
N(3)–C(15)	1.334(3)	N(6)–C(41)	1.331(3)	1.347	N(1)–C(5)–C(4)	122.64(15)	N(4)–C(31)–C(30)	122.66(15)	122.21
C(1)–C(2)	1.388(2)	C(27)–C(28)	1.388(3)	1.402	N(1)–C(5)–C(11)	116.32(16)	N(4)–C(31)–C(37)	116.19(15)	117.06
C(1)–C(6)	1.493(3)	C(27)–C(32)	1.496(3)	1.484	N(2)–C(6)–C(1)	116.03(16)	N(5)–C(32)–C(27)	116.08(17)	116.82
C(2)–C(3)	1.393(3)	C(28)–C(29)	1.390(3)	1.405	N(2)–C(6)–C(7)	122.72(18)	N(5)–C(32)–C(33)	122.83(18)	121.72
C(3)–C(4)	1.388(2)	C(29)–C(30)	1.392(2)	1.406	N(2)–C(10)–C(9)	124.1(2)	N(5)–C(36)–C(35)	124.1(2)	122.99
C(3)–C(16)	1.490(2)	C(29)–C(42)	1.489(2)	1.489	N(3)–C(11)–C(5)	115.78(18)	N(6)–C(37)–C(31)	115.78(16)	116.81
C(4)–C(5)	1.381(3)	C(30)–C(31)	1.381(2)	1.402	N(3)–C(11)–C(12)	122.49(18)	N(6)–C(37)–C(38)	122.49(16)	121.72
C(5)–C(11)	1.492(2)	C(31)–C(37)	1.493(2)	1.484	N(3)–C(15)–C(14)	124.9(3)	N(6)–C(41)–C(40)	124.7(2)	122.98
C(6)–C(7)	1.383(3)	C(32)–C(33)	1.379(3)	1.404					
C(7)–C(8)	1.378(3)	C(33)–C(34)	1.390(3)	1.396					
C(8)–C(9)	1.365(4)	C(34)–C(35)	1.364(4)	1.400					
C(9)–C(10)	1.368(4)	C(35)–C(36)	1.364(4)	1.398					
C(11)–C(12)	1.377(3)	C(37)–C(38)	1.378(3)	1.404					
C(12)–C(13)	1.388(3)	C(38)–C(39)	1.382(3)	1.396					
C(13)–C(14)	1.370(4)	C(39)–C(40)	1.373(3)	1.400					
C(14)–C(15)	1.357(5)	C(40)–C(41)	1.374(4)	1.399					
C(16)–C(25)	1.425(3)	C(42)–C(51)	1.432(2)	1.443					
C(16)–C(17)	1.373(2)	C(42)–C(43)	1.363(3)	1.387					
C(17)–C(18)	1.398(3)	C(43)–C(44)	1.398(3)	1.414					
C(18)–C(19)	1.365(3)	C(44)–C(45)	1.371(2)	1.381					
C(19)–C(20)	1.431(2)	C(45)–C(46)	1.425(3)	1.432					
C(19)–O(1)	1.357(2)	C(45)–O(2)	1.358(2)	1.389					
C(26)–O(1)	1.421(2)	C(52)–O(2)	1.415(2)	1.451					
C(20)–C(21)	1.408(3)	C(46)–C(47)	1.419(2)	1.421					
C(20)–C(25)	1.418(2)	C(46)–C(51)	1.421(2)	1.438					
C(21)–C(22)	1.366(3)	C(47)–C(48)	1.360(3)	1.381					
C(22)–C(23)	1.398(3)	C(48)–C(49)	1.394(3)	1.415					
C(23)–C(24)	1.354(3)	C(49)–C(50)	1.365(3)	1.382					
C(24)–C(25)	1.422(2)	C(50)–C(51)	1.410(2)	1.425					
1–R⁷									
N(1)–C(1)		1.3423(17)		1.355	C(1)–N(1)–C(5)		117.19(11)		118.56
N(1)–C(5)		1.3427(18)		1.355	C(10)–N(2)–C(6)		117.62(13)		118.75
N(2)–C(6)		1.3401(18)		1.359	C(15)–N(3)–C(11)		117.32(15)		118.75
N(2)–C(10)		1.3362(19)		1.349	N(1)–C(1)–C(2)		122.79(12)		122.18
N(3)–C(11)		1.3328(19)		1.359	N(1)–C(1)–C(6)		117.33(11)		116.85
N(3)–C(15)		1.333(2)		1.349	N(1)–C(5)–C(4)		123.02(12)		122.18
N(4)–C(19)		1.3748(17)		1.383	N(1)–C(5)–C(11)		116.31(11)		116.85
N(4)–C(22)		1.4334(19)		1.466	N(2)–C(6)–C(1)		116.29(11)		116.99
N(4)–C(23)		1.4358(19)		1.466	N(2)–C(6)–C(7)		121.82(13)		121.59
C(1)–C(2)		1.3836(18)		1.400	N(2)–C(10)–C(9)		123.67(16)		123.00
C(1)–C(6)		1.4876(19)		1.486	N(3)–C(11)–C(5)		116.35(12)		116.99
C(2)–C(3)		1.3926(18)		1.409	N(3)–C(11)–C(12)		122.01(13)		121.59
C(3)–C(4)		1.3894(18)		1.409	N(3)–C(15)–C(14)		124.11(18)		123.00
C(3)–C(16)		1.4772(17)		1.478					
C(4)–C(5)		1.3889(18)		1.400					
C(5)–C(11)		1.4917(18)		1.486					
C(6)–C(7)		1.3795(18)		1.404					
C(7)–C(8)		1.378(2)		1.397					
C(8)–C(9)		1.361(3)		1.400					
C(9)–C(10)		1.371(2)		1.399					
C(11)–C(12)		1.3777(19)		1.404					
C(12)–C(13)		1.376(2)		1.398					
C(13)–C(14)		1.359(3)		1.400					
C(14)–C(15)		1.366(3)		1.399					
C(16)–C(21)		1.3897(18)		1.411					
C(16)–C(17)		1.3908(19)		1.411					
C(17)–C(18)		1.3762(19)		1.391					
C(18)–C(19)		1.3978(19)		1.421					
C(19)–C(20)		1.4007(19)		1.421					
C(20)–C(21)		1.3763(18)		1.391					
1–R⁸									
N(1)–C(1)		1.3415(16)		1.353	C(1)–N(1)–C(5)		118.22(17)		118.9
N(1)–C(1)#1		1.3415(16)		1.353	C(4)–N(2)–C(8)		117.37(14)		118.8
N(2)–C(4)		1.3358(18)		1.358	C(11)–N(3)–C(11)		115.55(19)		117.3
N(2)–C(8)		1.3381(19)		1.347	N(1)–C(1)–C(2)		122.49(13)		122.1
N(3)–C(11)		1.3309(18)		1.352	N(1)–C(1)–C(4)		116.21(13)		117.2
N(3)–C(11)#1		1.3309(18)		1.352	N(2)–C(4)–C(1)		116.45(13)		116.7
C(1)–C(2)		1.388(2)		1.402	N(2)–C(4)–C(5)		122.19(13)		121.8
C(1)–C(4)		1.4875(19)		1.484	N(2)–C(8)–C(7)		124.00(16)		124.7
C(2)–C(3)		1.3895(17)		1.404	N(3)–C(11)–C(10)		124.29(15)		123.9

C(3)–C(2)#1	1.3895(17)	1.404			
C(3)–C(9)	1.490(3)	1.485			
C(4)–C(5)	1.387(2)	1.404			
C(5)–C(6)	1.378(2)	1.396			
C(6)–C(7)	1.367(2)	1.400			
C(7)–C(8)	1.368(2)	1.399			
C(9)–C(10)#1	1.3843(17)	1.407			
C(9)–C(10)	1.3843(17)	1.407			
C(10)–C(11)	1.371(2)	1.396			
		1–R^{14}			
N(1)–C(1)	1.350(3)	1.355	C(1)–N(1)–C(5)	119.2(2)	118.87
N(1)–C(5)	1.351(3)	1.355	C(10)–N(2)–C(6)	116.6(3)	118.72
N(2)–C(6)	1.356(3)	1.359	C(15)–N(3)–C(11)	115.8(3)	118.71
N(2)–C(10)	1.337(4)	1.349	N(1)–C(1)–C(2)	121.3(2)	122.17
N(3)–C(11)	1.333(3)	1.359	N(1)–C(1)–C(6)	116.6(3)	117.01
N(3)–C(15)	1.304(4)	1.349	N(1)–C(5)–C(4)	120.9(2)	122.17
C(1)–C(2)	1.350(4)	1.399	N(1)–C(5)–C(11)	117.4(2)	117.00
C(1)–C(6)	1.481(4)	1.485	N(2)–C(6)–C(1)	116.9(2)	116.85
C(2)–C(3)	1.377(4)	1.407	N(2)–C(6)–C(7)	122.2(2)	121.71
C(3)–C(4)	1.392(4)	1.406	N(2)–C(10)–C(9)	122.8(3)	122.94
C(3)–C(16)	1.449(4)	1.452	N(3)–C(11)–C(5)	117.2(2)	116.87
C(4)–C(5)	1.364(4)	1.400	N(3)–C(11)–C(12)	121.5(3)	121.69
C(5)–C(11)	1.481(4)	1.485	N(3)–C(15)–C(14)	123.8(3)	122.97
C(6)–C(7)	1.372(4)	1.404			
C(7)–C(8)	1.340(4)	1.397			
C(8)–C(9)	1.337(4)	1.400			
C(9)–C(10)	1.357(4)	1.399			
C(11)–C(12)	1.351(4)	1.404			
C(12)–C(13)	1.296(4)	1.397			
C(13)–C(14)	1.290(5)	1.400			
C(14)–C(15)	1.318(5)	1.399			
C(16)–O(1)	1.359(5)	1.405			
C(16)–C(17)	1.321(12)	1.375			
C(17)–C(18)	1.485(19)	1.436			
C(18)–C(19)	1.23(2)	1.366			

Table S2. Short intra– and intermolecular contacts detected in the structures **1–R^{3}**, **1–R^{7}** and **1–R^{14}**.

D—H•••A	**D—H**	**H•••A**	**D•••A [Å]**	**D—H•••A [°]**
		1–R^{3}		
C(2)–H(2)•••N(2)	0.93	2.47	2.790(2)	100.00
C(4)–H(4)•••N(3)	0.93	2.47	2.791(3)	100.40
C(7)–H(7)•••N(1)	0.93	2.50	2.809(3)	99.6
C(21)–H(21)•••O(1)	0.93	2.42	2.736(3)	100.00
C(28)–H(28)•••N(5)	0.93	2.48	2.798(3)	99.9
C(30)–H(30)•••N(6)	0.93	2.47	2.794(2)	100.20
C(38)–H(38)•••N(4)	0.93	2.51	2.814(2)	99.6
		1–R^{7}		
C(2)–H(2)•••N(2)	0.93	2.46	2.7829(18)	100.40
		1–R^{14}		
C(2)–H(2)•••N(2)	0.93	2.49	2.815(4)	100.70
C(4)–H(4)•••O(1)	0.93	2.51	2.827(6)	99.9
C(4)–H(4)•••N(3)	0.93	2.50	2.809(4)	99.8
C(7)–H(7)•••N(1)	0.93	2.48	2.794(4)	99.6
C(12)–H(12)•••N(1)	0.93	2.50	2.806(4)	99.7

Table S3. Calculated Onsager cavity radius (*a*).

	a [Å]		*a* [Å]
1–R[1]	6.14	**1–R[9]**	5.24
1–R[2]	5.86	**1–R[10]**	5.45
1–R[3]	5.57	**1–R[11]**	5.24
1–R[4]	5.65	**1–R[12]**	5.83
1–R[5]	5.51	**1–R[13]**	5.72
1–R[6]	5.50	**1–R[14]**	5.65
1–R[7]	5.91	**1–R[15]**	5.50
1–R[8]	5.41	**1–R[16]**	5.37

Table S4. Electrochemical properties and optical band gaps of the compounds **1–R[1–16]**.

Compound	CV [b]					E_g^{opt} [eV] [a]
	E_{red} [V]	E_{ox} [V]	E_{HOMO} [eV]	E_{LUMO} [eV]	Eg [eV]	
1–R[1]	–2.29	0.78	–5.88	–2.81	3.06	2.93
1–R[2]	–2.27	1.18	–6.28	–2.83	3.45	3.41
1–R[3]	–2.16	0.90 1.23	–6.00	–2.94	3.06	3.06
1–R[4]	–2.28	1.19	–6.29	–2.82	3.48	3.48
1–R[5]	–2.21 –2.46	1.25	–6.35	–2.89	3.46	3.48
1–R[6]	–2.11	1.08	–6.18	–2.99	3.18	2.90
1–R[7]	–2.26	0.36 0.60	–5.46	–2.84	2.61	2.64
1–R[8]	–2.07 –2.39	1.00	–6.10	–3.03	3.07	3.48
1–R[9]	–2.20	1.20	–6.30	–2.90	3.40	3.50
1–R[10]	–2.36	0.73 1.00	–5.83	–2.74	3.09	2.93
1–R[11]	–2.18	1.15	–6.25	–2.92	3.26	3.44
1–R[12]	–2.16 –2.47	0.76 1.08	–5.86	–2.95	2.91	2.85
1–R[13]	–2.02 –2.40	1.16	–6.26	–3.08	3.18	3.33
1–R[14]	–2.20	0.94	–6.04	–2.90	3.14	3.46
1–R[15]	–2.14 –2.38	0.81	–5.91	–2.96	2.95	3.09
1–R[16]	–2.21	1.16	–6.26	–2.89	3.37	3.26

a. $E_g^{opt} = 1241/\lambda_{em}$

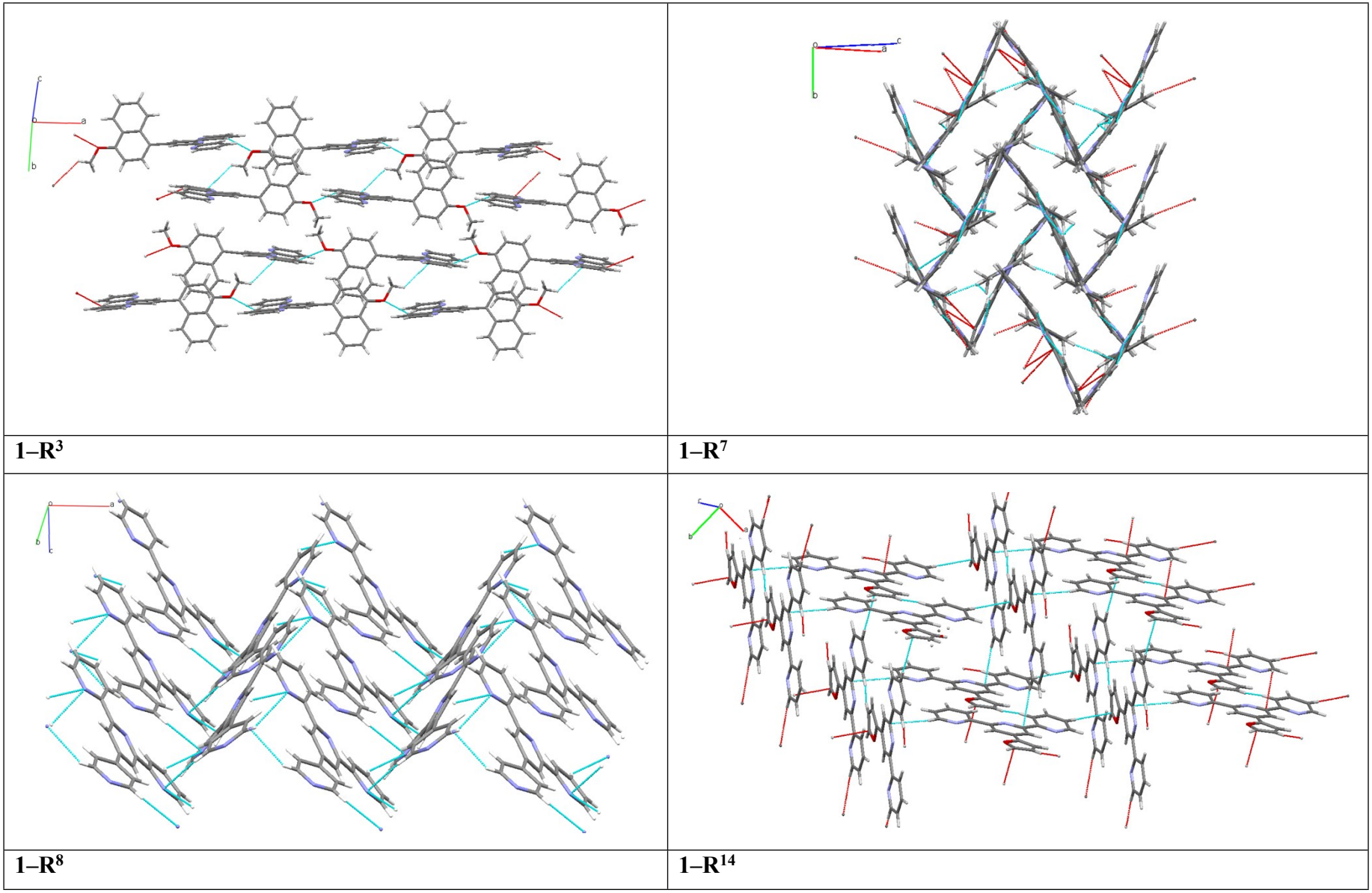
b. Measured in CH_2Cl_2 solution, GC as working electrode, HOMO= –5.1– E_{ox}; LUMO= –5.1–E_{red}; scan rate 100 [mV/s]

Table S5. The energies and characters of the selected calculated transitions assigned to the lowest experimental absorption bands of the compounds **1–R[1–16]** (in acetonitrile)

		λ_{abs} [nm]	Calculated transitions			
			λ [nm]	*f*	The most important orbital excitations	Character
1–R[1]	CIS(D)	385.4	484.4	0.0177	H→L (19%), H→L+2 (81%)	$\pi_R \rightarrow \pi^*_{terpy}$
			391.7	0.1684	H→L (70%), H→L+2 (18%)	$\pi_R \rightarrow \pi^*_R$
	TD	385.4	389.3	0.1542	H→L (87%)	$\pi_R \rightarrow \pi^*_R$
			369.3	0.0300	H→L+2 (87%)	$\pi_R \rightarrow \pi^*_{terpy}$
1–R[2]	CIS(D)	288.1	374.0	0.3403	H→L (88%)	$\pi_R \rightarrow \pi^*_{terpy}$
			339.3	0.1276	H–2→L (78%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			315.9	0.2246	H→L+2 (58%), H→L+3 (33%)	$\pi_R \rightarrow \pi^*_{terpy}$
			310.5	0.1494	H–6→L+1 (29%), H–2→L+1 (46%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			307.8	0.0557	H–6→L+1 (70%), H–2→L+1 (17%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
	TD	288.1	311.9	0.8069	H→L (97%)	$\pi_R \rightarrow \pi^*_{terpy}$
			294.5	0.2528	H–1→L (55%), H→L+1 (41%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_{terpy}$
			278.5	0.3465	H–1→L+1 (89%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
1–R[3]	CIS(D)	325.9	438.6	0.1203	H→L (63%), H→L+1 (27%)	$\pi_R \rightarrow \pi^*_{terpy}$
			333.7	0.1198	H–2→L (52%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			324.0	0.1458	H→L+2 (28%) H–4→L+1 (25%), H–4→L (19%)	$\pi_R \rightarrow \pi^*_R$, $\pi_{terpy} \rightarrow \pi^*_{terpy}$
			320.2	0.1512	H–4→L (29%), H–4→L+1 (16%), H→L+2 (24%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_R$,
	TD	325.9	350.3	0.2308	H→L (90%)	$\pi_R \rightarrow \pi^*_{terpy}$
		289.0	298.4	0.1038	H–2→L (35%), H–1→L (19%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
1–R[4]	CIS(D)	329.6	346.7	0.0544	H–3→L+1 (39%), H–1→L (55%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_{terpy}$
			320.0	0.1175	H–3→L+1 (52%), H–1→L (26%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_{terpy}$
			319.3	0.2125	H–3→L (73%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
	TD	329.6	306.1	0.1778	H→L (83%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
		289.0	278.4	0.5440	H→L+1 (79%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			272.8	0.2344	H–1→L (83%)	$\pi_R \rightarrow \pi^*_{terpy}$
			271.4	0.3275	H–1–>L+1 (80%)	$\pi_R \rightarrow \pi^*_{terpy}$
1–R[5]	CIS(D)	331.8	327.5	0.2512	H–3→L (80%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			325.4	0.1241	H–3→L+1 (43%), H–1→L (37%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_{terpy}$
			308.9	0.1895	H–1→L+1 (69%)	$\pi_R \rightarrow \pi^*_{terpy}$
	TD	331.8	306.6	0.1699	H→L (81%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
		288.6	280.1	0.7924	H–1→L (52%), H→L+1 (40%)	$\pi_R \rightarrow \pi^*_{terpy}$
			274.5	0.2801	H–1→L+1 (80%)	$\pi_R \rightarrow \pi^*_{terpy}$
1–R[6]	CIS(D)	343.4	**344.7**	**0.0738**	**H–3→L+1 (32%), H–1→L (62%)**	$\boldsymbol{\pi_{terpy} \rightarrow \pi^*_{terpy}}$
			316.3	0.0944	H–3→L+1 (40%), H–3→L (14%), H–1→L (13%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			315.4	0.1250	H–4→L (11%), H–3→L (44%), H–3→L+1 (14%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
	TD	343.4	305.9	0.1992	H→L (85%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
		287.6	277.4	0.2426	H–3→L (28%), H→L+1 (54%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			276.7	0.1376	H–3→L (40%), H→L+1 (39%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			267.8	0.2686	H–1→L (82%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			266.8	0.3817	H–1–>L+1 (76%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
1–R[7]	CIS(D)	432.3	494.7	0.2217	H→L+1 (91%)	$\pi_R \rightarrow \pi^*_{terpy}$
			418.8	0.0653	H→L+2 (94%)	$\pi_R \rightarrow \pi^*_{terpy}$
		351.9	330.7	0.1204	H–2→L+1 (74%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$
			325.9	0.7213	H→L+4 (70%)	$\pi_R \rightarrow \pi^*_{terpy}$
	TD	432.3	400.7	0.0004	H→L (99%)	$\pi_R \rightarrow \pi^*_{terpy}$
		351.9	385.1	0.4182	H→L+1 (99%)	$\pi_R \rightarrow \pi^*_{terpy}$
1–R[8]	CIS(D)	314.7	352.3	0.0972	H–3→L (67%), H–1→L (18%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_{terpy}$
			311.0	0.0697	H–6→L (16%), H–5→L (29%), H–3→L+1 (31%), H–1→L+1 (14%)	$\pi_{terpy} \rightarrow \pi^*_{terpy}$, $\pi_R \rightarrow \pi^*_{terpy}$

			298.8	0.0348	H–2→L+2 (52%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
	TD	314.7	312.4	0.1961	H→L (92%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
1–R[9]	CIS(D)	327.4	358.0	0.0986	H–1→L (65%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			313.3	0.0664	H–6→L (33%), H–1→L+1 (42%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			301.7	0.2189	H–4→L+1 (47%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			300.8	0.0863	H–6→L+1 (24%), H–1→L+2 (34%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
	TD	327.4	317.1	0.1839	H→L (90%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
1–R[10]	CIS(D)	378.4	401.2	0.1598	H→L+1 (78%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			354.9	0.0565	H→L+2 (91%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
	TD	378.4	353.2	0.0021	H→L (59%), H→L+1 (37%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			335.28	0.3172	H→L (39%), H→L+1 (60%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
1–R[11]	CIS(D)	343.4	358.1	0.0310	H–2→L+1 (33%), H–1→L (33%), H–1→L+1 (15%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R}\rightarrow\pi^*_{terpy}$
			330.6	0.0655	H–1→L (37%), H–2→L (20%), H–5→L (10%)	$\pi_{R}\rightarrow\pi^*_{terpy}$, $\pi_{terpy}\rightarrow\pi^*_{terpy}$
			322.8	0.1509	H–2→L+1 (43%), H–2→L (19%), H–1→L (11%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R}\rightarrow\pi^*_{terpy}$,
	TD	343.4	314.8	0.1181	H–1→L+1 (21%), H→L (75%)	$\pi_{R}\rightarrow\pi^*_{terpy}$, $\pi_{terpy}\rightarrow\pi^*_{terpy}$
1–R[12]	CIS(D)	354.6	427.7	0.6143	H→L (74%)	$\pi_{R}\rightarrow\pi^*_{R/terpy}$
			368.4	0.0791	H–2→L (86%)	$\pi_{terpy}\rightarrow\pi^*_{R/terpy}$
			360.5	0.3430	H→L+3 (49%), H→L+2 (39%),	$\pi_{R}\rightarrow\pi^*_{terpy}$
			337.1	0.5199	H→L+3 (42%), H→L+2 (22%),	$\pi_{R}\rightarrow\pi^*_{terpy}$
	TD	354.6	378.9	0.9871	H→L (99%)	$\pi_{R}\rightarrow\pi^*_{R/terpy}$
			351.4	0.0017	H→L+1 (87%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
1–R[13]	CIS(D)	315.0	354.7	0.3611	H–2→L (44%), H–4→L (23%), H→L (11%)	$\pi_{R/terpy}\rightarrow\pi^*_{terpy}$, $\pi_{terpy}\rightarrow\pi^*_{terpy}$
			341.6	0.1075	H–2→L+1 (30%), H–4→L (29%),	$\pi_{R/terpy}\rightarrow\pi^*_{terpy}$, $\pi_{terpy}\rightarrow\pi^*_{terpy}$
			321.5	0.228	H→L+2 (54%), H→L+3 (30%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			314.4	0.0706	H–6→L (50%), H–4→L+1 (18%), H→L+3 (10%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R}\rightarrow\pi^*_{terpy}$
			302.0	0.0592	H–2→L+2 (39%), H–6→L+1 (23%)	$\pi_{R/terpy}\rightarrow\pi^*_{terpy}$
	TD	315.0	326.9	0.1397	H–1→L (39%), H→L+1 (41%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R}\rightarrow\pi^*_{terpy}$
			311.8	0.1416	H–3→L (56%), H–2→L (27%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R/terpy}\rightarrow\pi^*_{terpy}$
1–R[14]	CIS(D)	342.7	347.4	0.2045	H→L (70%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			331.9	0.1941	H–2→L (70%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			312.3	0.0573	H→L+2 (71%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			308.1	0.2242	H–2→L+1 (66%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
	TD	342.7	320.8	0.0366	H–1→L (41%), H→L+1 (57%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R}\rightarrow\pi^*_{R}$
		292.5	304.2	0.5190	H→L (97%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			291.9	0.3563	H–1→L (56%), H→L+1 (42%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$, $\pi_{R}\rightarrow\pi^*_{R}$
			276.5	0.2544	H–1→L+1 (93%)	$\pi_{terpy}\rightarrow\pi^*_{R}$

1–R[15]	CIS(D)	350.5	327.7	0.1113	H–2→L+1 (73%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			310.4	0.1664	H–2→L (58%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
	TD	350.5	337.4	0.0411	H→L (99%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			327.9	0.0343	H→L+1 (99%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
1–R[16]	CIS(D)	313.0	418.1	0.1915	H→L (68%), H→L+2 (23%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			371.0	0.0813	H→L+2 (52%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			344.5	0.0844	H–2→L (64%), H–4→L+1 (29%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			325.1	0.0708	H–4→L (57%), H–4→L+1 (13%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
	TD	313.0	353.2	0.4717	H→L (96%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			303.1	0.2749	H–1→L (89%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$
			291.9	0.1808	H→L+2 (94%)	$\pi_{R}\rightarrow\pi^*_{terpy}$
			279.8	0.1788	H–1→L+1 (63%)	$\pi_{terpy}\rightarrow\pi^*_{terpy}$



1–R^3

1–R^7

1–R^8

1–R^{14}

Figure S1: View of the packing of **1–R^3**, **1–R^7**, **1–R^8** and **1–R^{14}** showing short intra– and intermolecular C—H•••O and C—H•••N contacts.

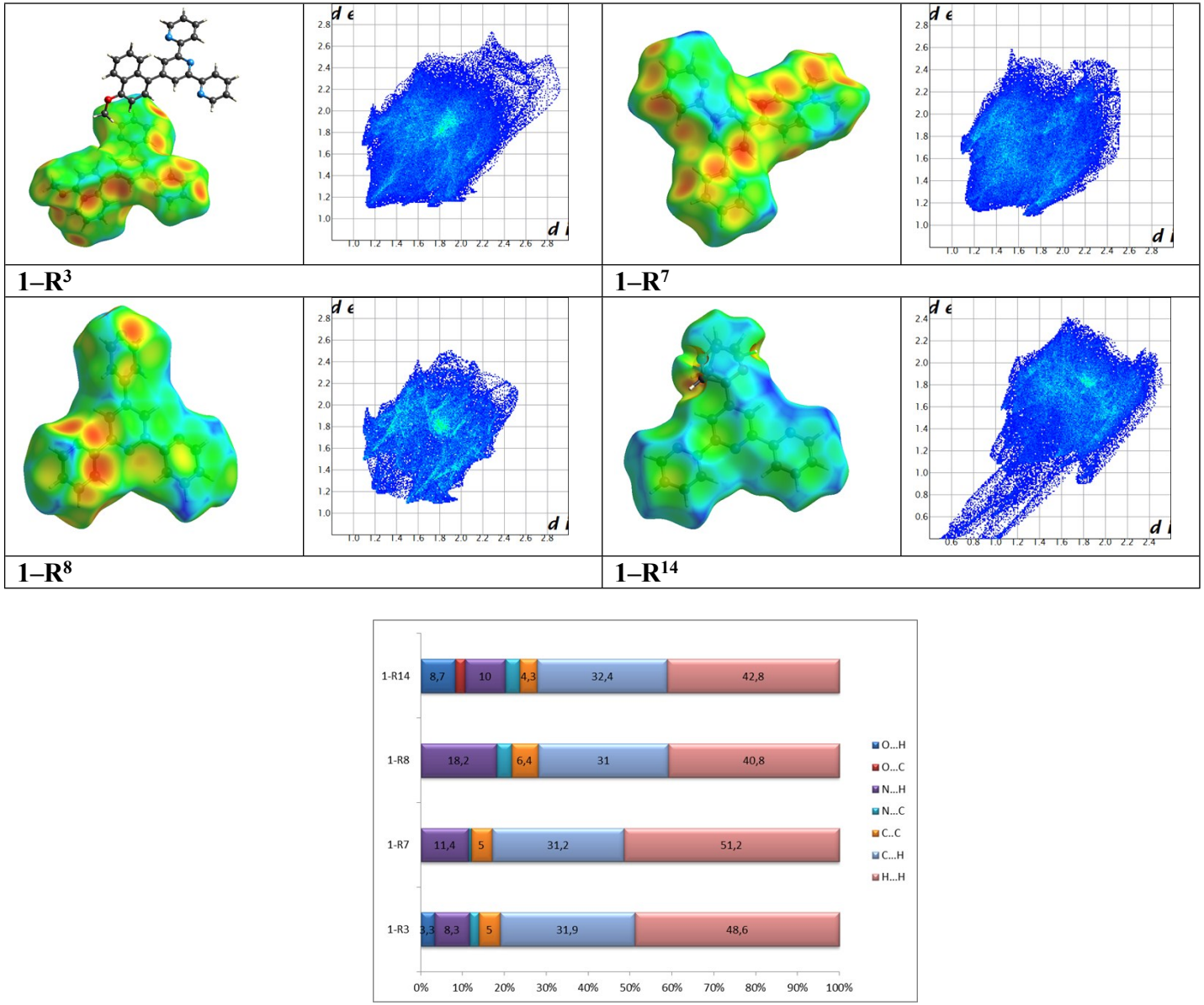
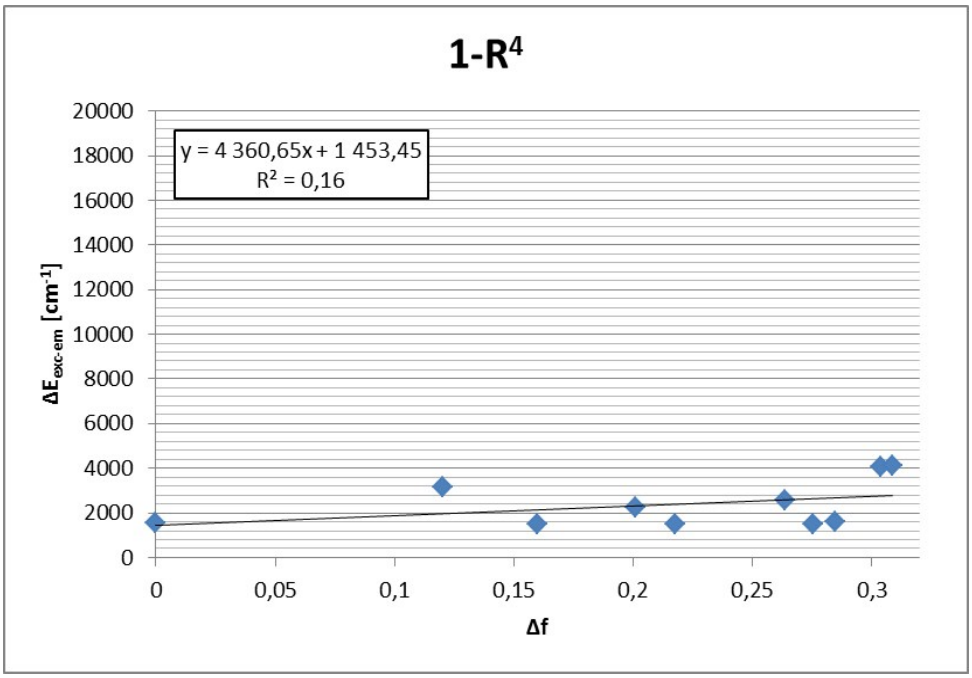


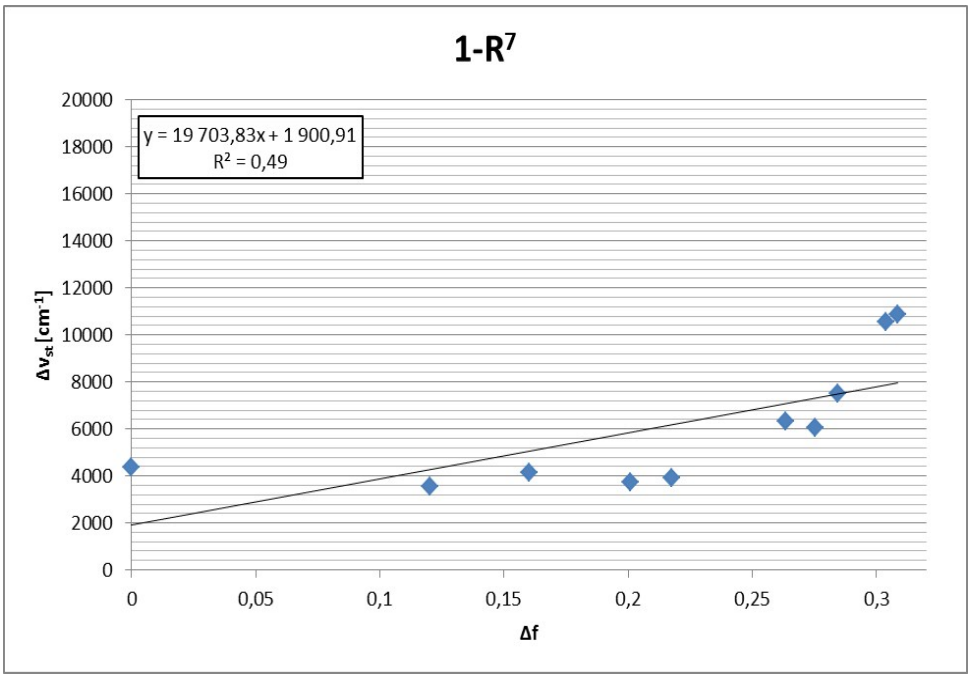
Figure S2. Hirshfeld surfaces, 2D fingerprint plots and percentage contributions to the Hirshfeld surface area for the various close intermolecular contacts for molecules of **1–R^3**, **1–R^7** and **1–R^{14}** compounds.

Figure S3. Plot of difference between absorption and fluorescence wavenumber $\Delta\bar{\nu}_{st}$ *vs.* solvent polarity parameter Δf for **1–R⁴**.



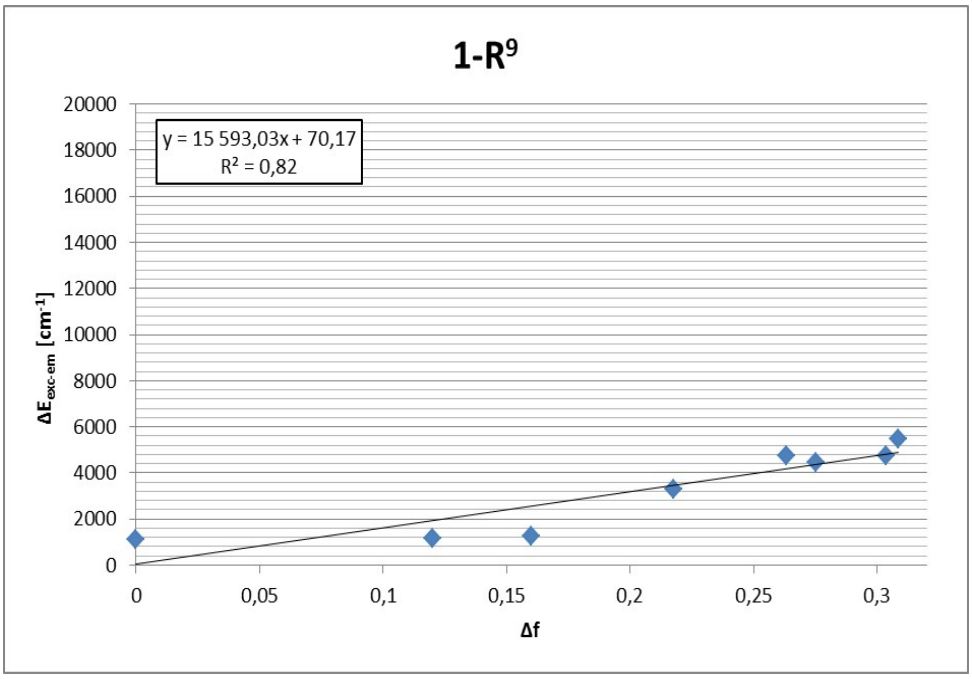
Solvent	Δf
Methanol	0.309
Acetonitryle	0.304
Acetone	0.285
N.N–dimethylformamide	0.275
Dimethyl sulfoxide	0.264
Dichloromethane	0.218
Ethyl acetate	0.201
Diethyl ether	0.160
Dipropyl ether	0.120
Cyclohexane	0.0

Figure S4. Plot of difference between absorption and fluorescence wavenumber $\Delta\bar{\nu}_{st}$ *vs.* solvent polarity parameter Δf for **1–R⁷**.



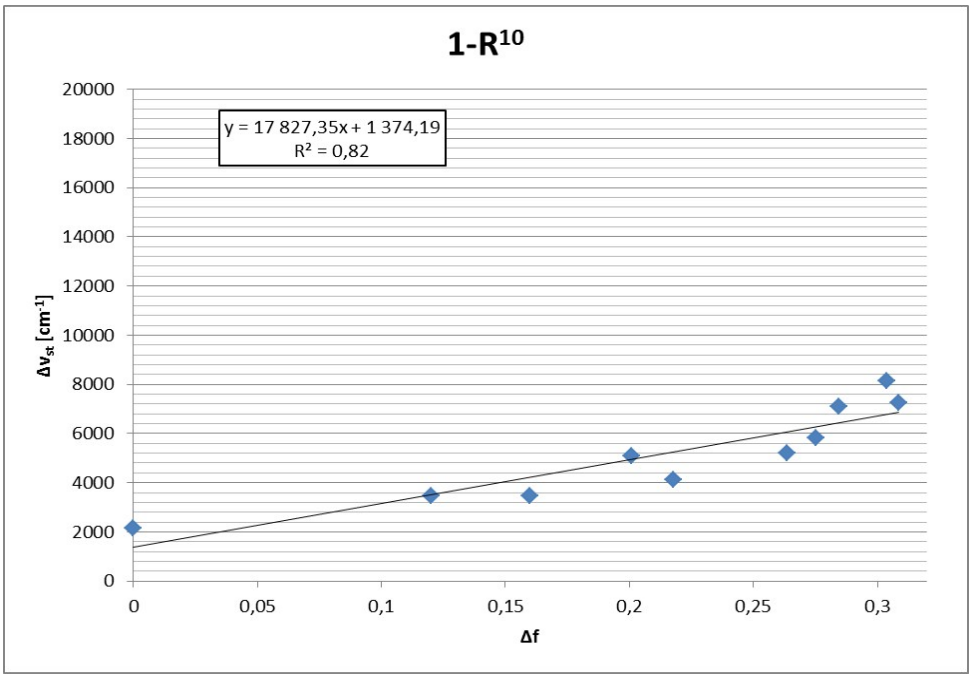
Solvent	Δf
Methanol	0.309
Acetonitryle	0.304
Acetone	0.285
N.N–dimethylformamide	0.275
Dimethyl sulfoxide	0.264
Dichloromethane	0.218
Ethyl acetate	0.201
Diethyl ether	0.160
Dipropyl ether	0.120
Cyclohexane	0.0

Figure S5. Plot of difference between absorption and fluorescence wavenumber $\Delta\bar{\nu}_{st}$ *vs.* solvent polarity parameter Δf for **1–R^9**.



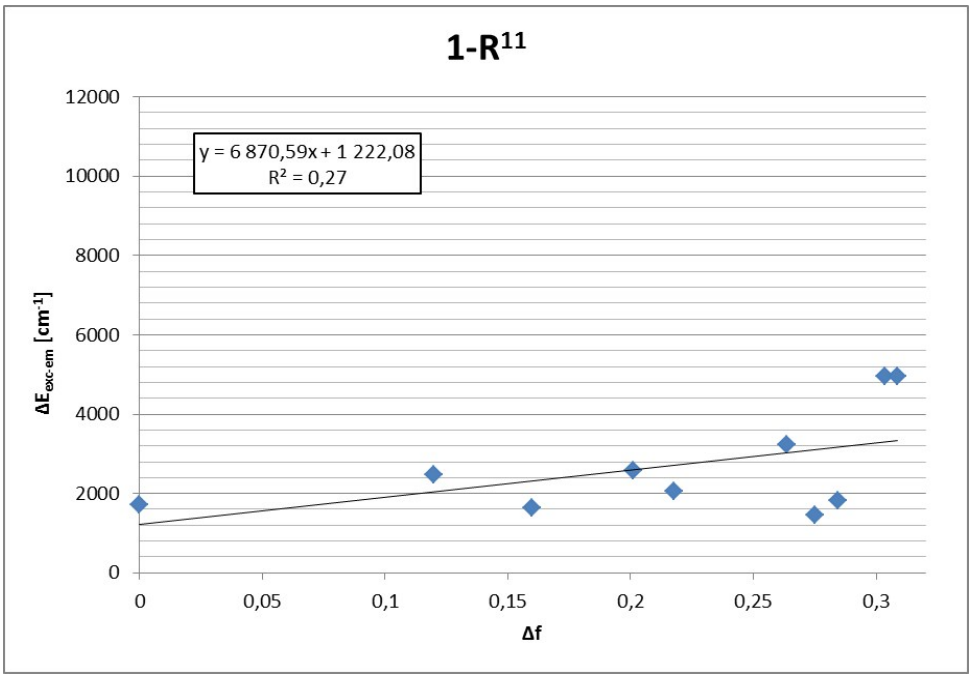
Solvent	Δf
Methanol	0.309
Acetonitryle	0.304
Acetone	0.285
N.N–dimethylformamide	0.275
Dimethyl sulfoxide	0.264
Dichloromethane	0.218
Ethyl acetate	0.201
Diethyl ether	0.160
Dipropyl ether	0.120
Cyclohexane	0.0

Figure S6. Plot of difference between absorption and fluorescence wavenumber $\Delta\bar{\nu}_{st}$ *vs.* solvent polarity parameter Δf for **1–R^{10}**.



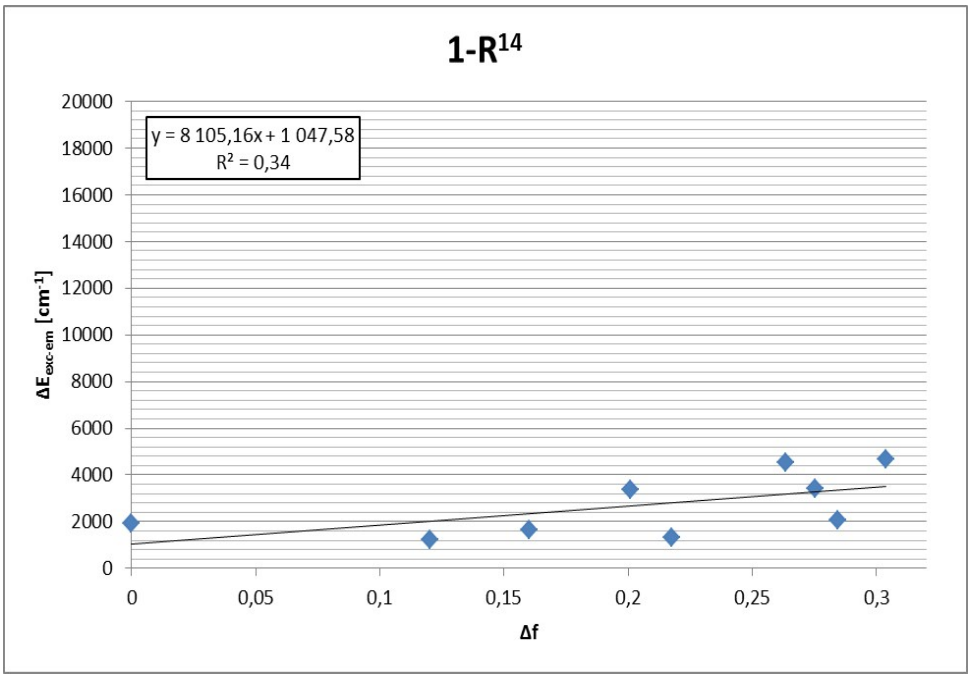
Solvent	Δf
Methanol	0.309
Acetonitryle	0.304
Acetone	0.285
N.N–dimethylformamide	0.275
Dimethyl sulfoxide	0.264
Dichloromethane	0.218
Ethyl acetate	0.201
Diethyl ether	0.160
Dipropyl ether	0.120
Cyclohexane	0.0

Figure S7. Plot of difference between absorption and fluorescence wavenumber $\Delta\bar{\nu}_{st}$ *vs.* solvent polarity parameter Δf for **1–R^{11}**.



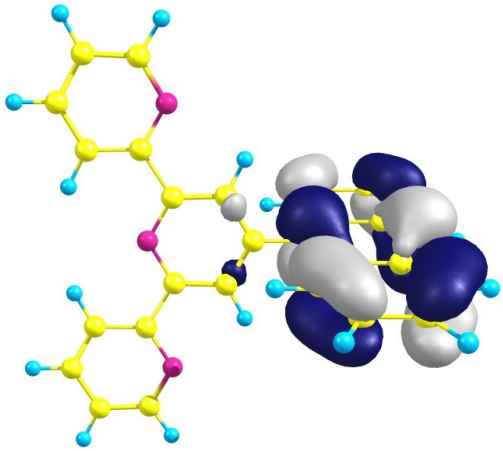
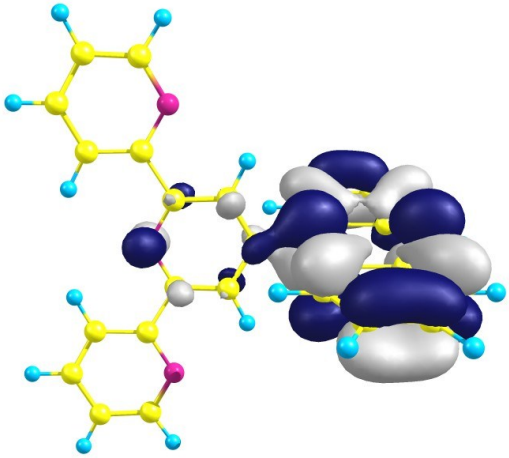
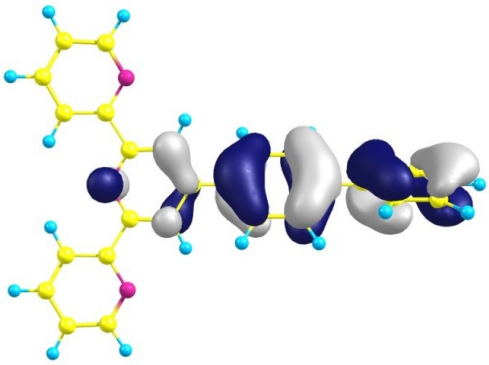
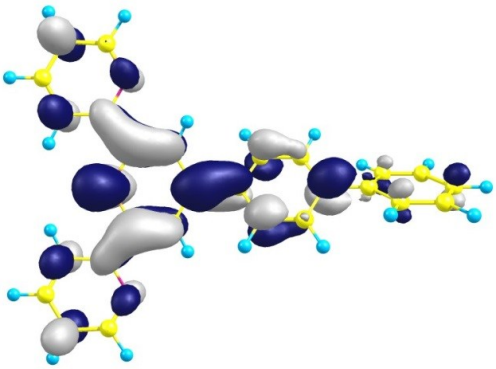
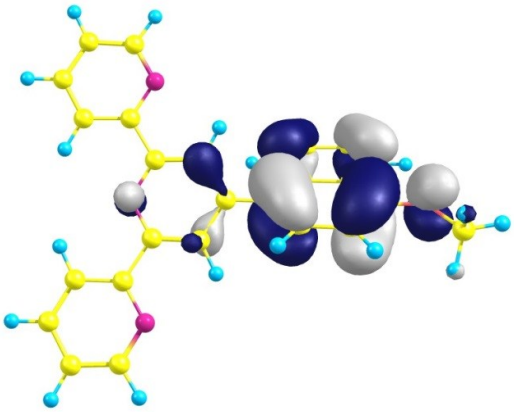
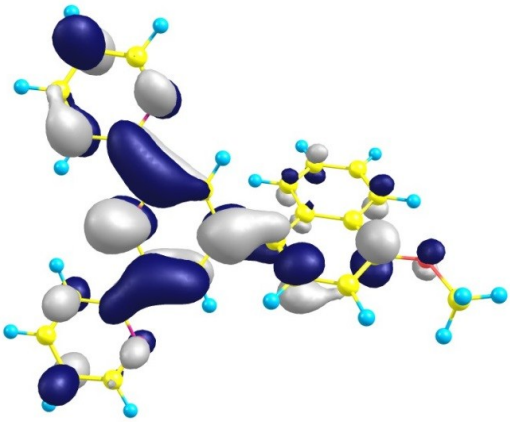
Solvent	Δf
Methanol	0.309
Acetonitryle	0.304
Acetone	0.285
N.N–dimethylformamide	0.275
Dimethyl sulfoxide	0.264
Dichloromethane	0.218
Ethyl acetate	0.201
Diethyl ether	0.160
Dipropyl ether	0.120
Cyclohexane	0.0

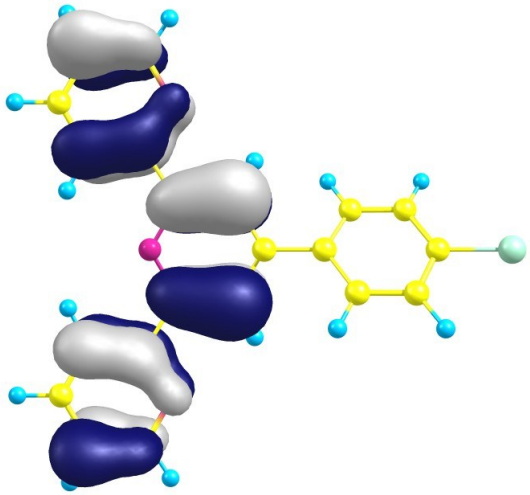
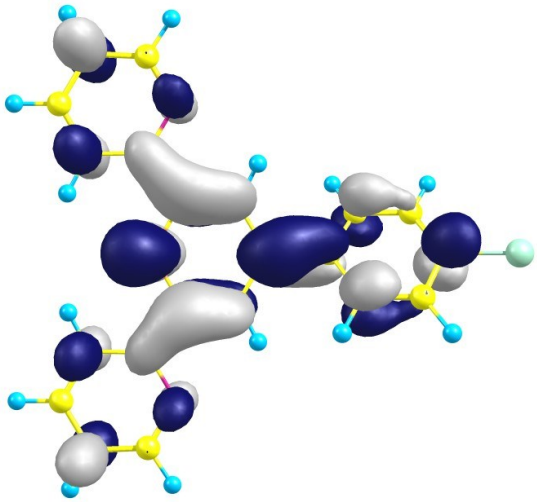
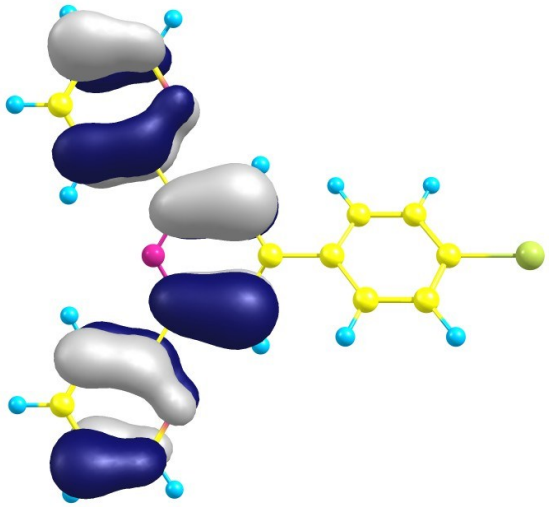
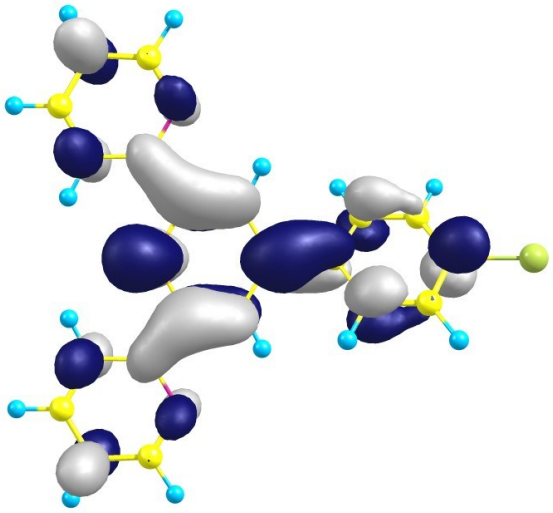
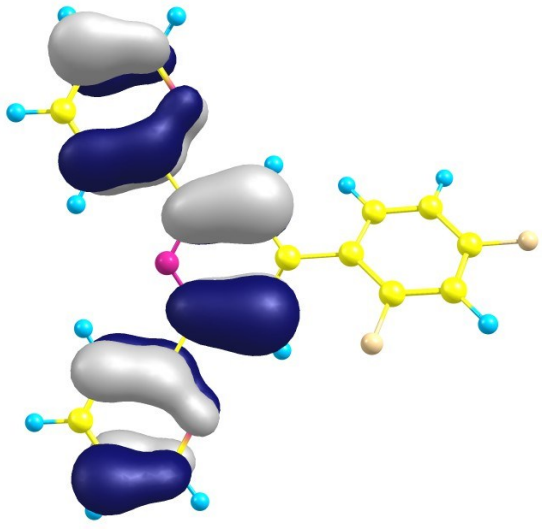
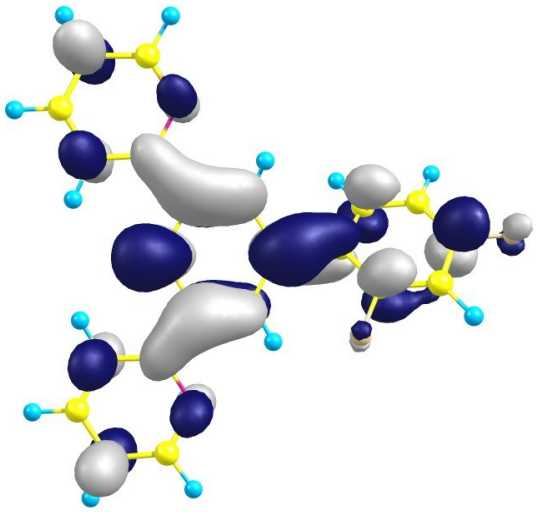
Figure S8. Plot of difference between absorption and fluorescence wavenumber $\Delta\bar{\nu}_{st}$ *vs.* solvent polarity parameter Δf for **1–R^{14}**.

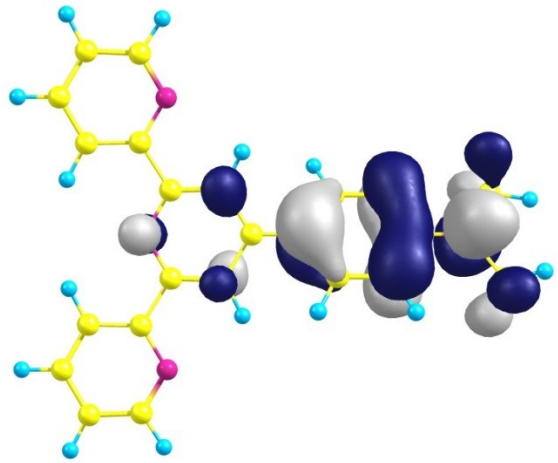
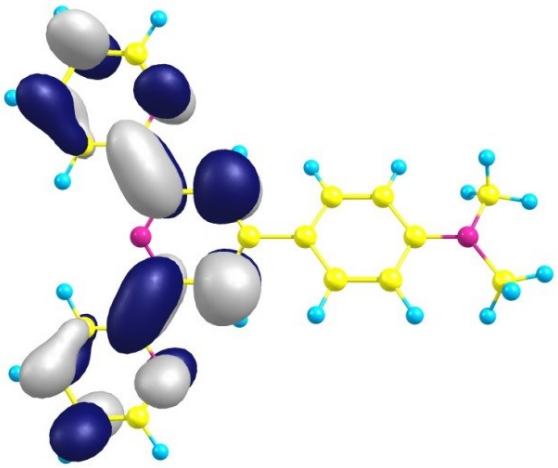
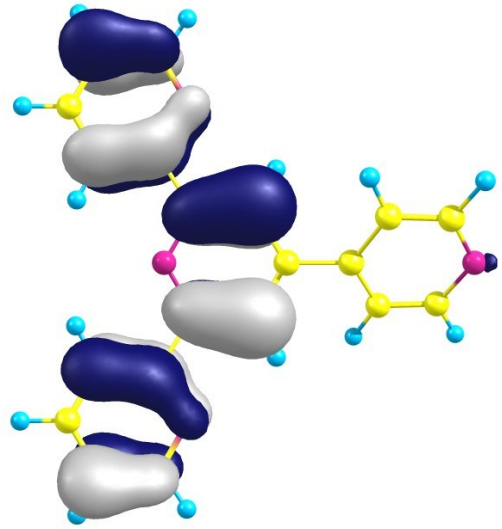
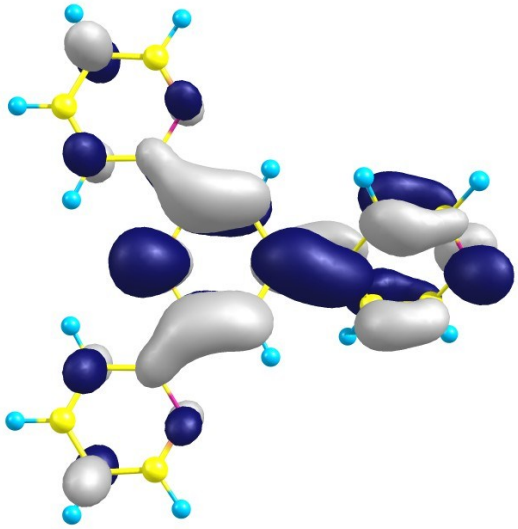
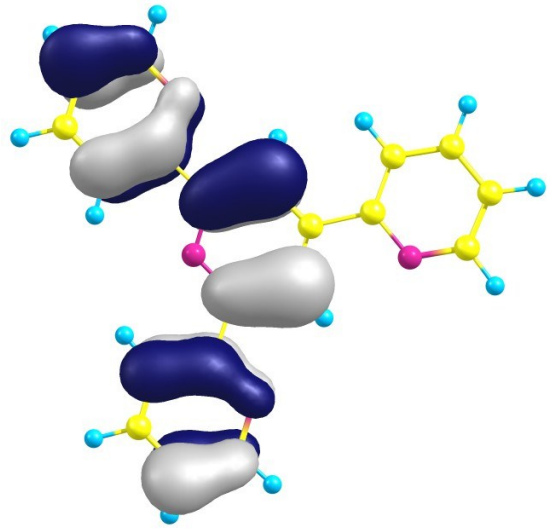
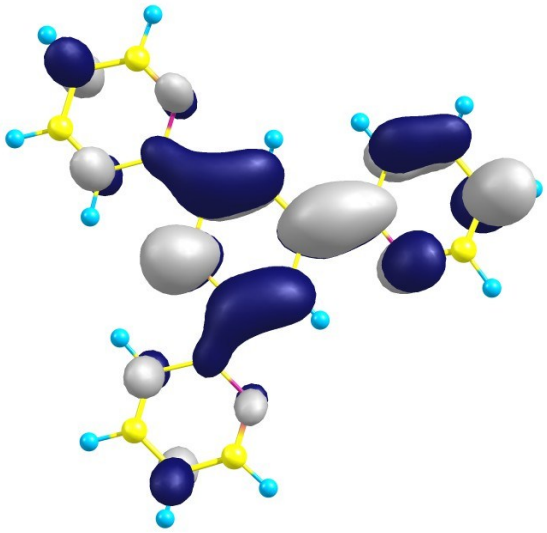


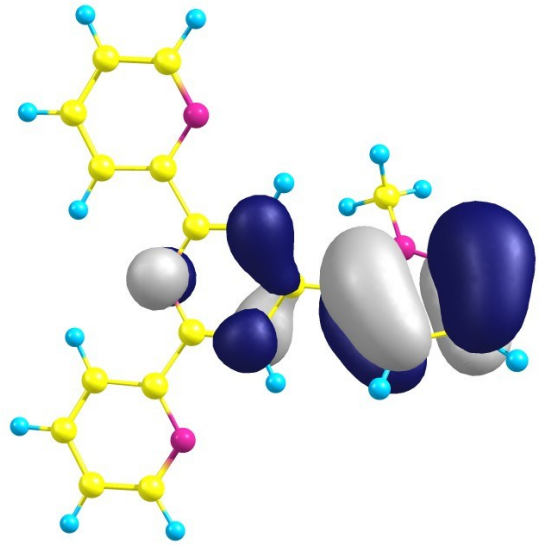
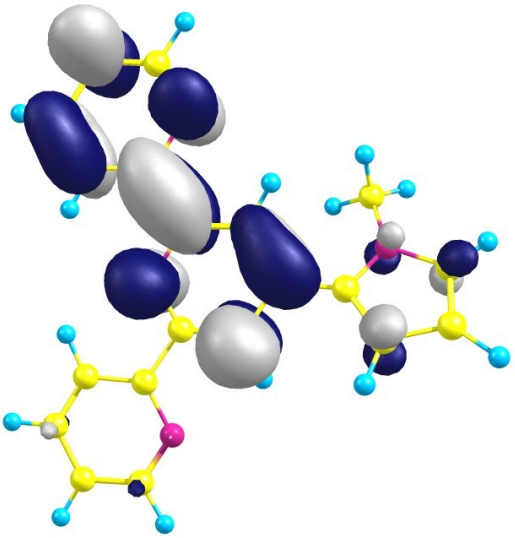
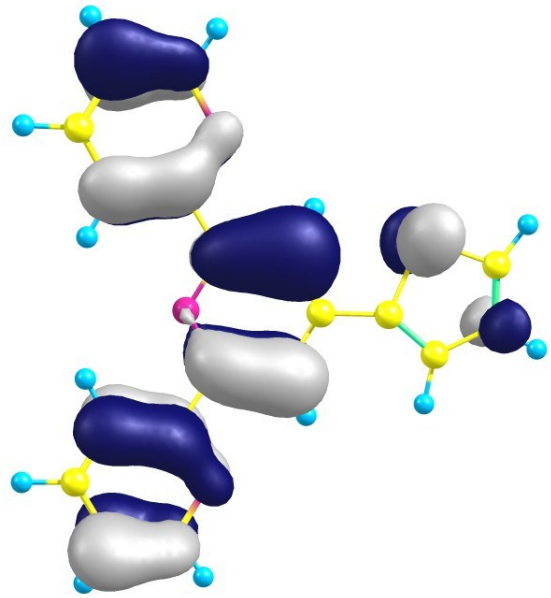
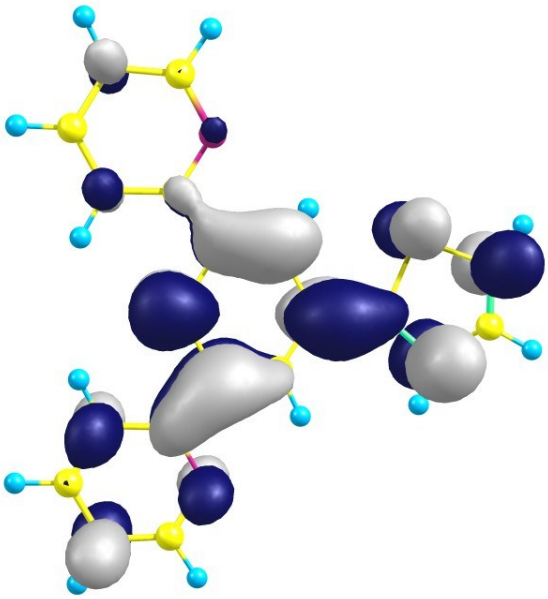
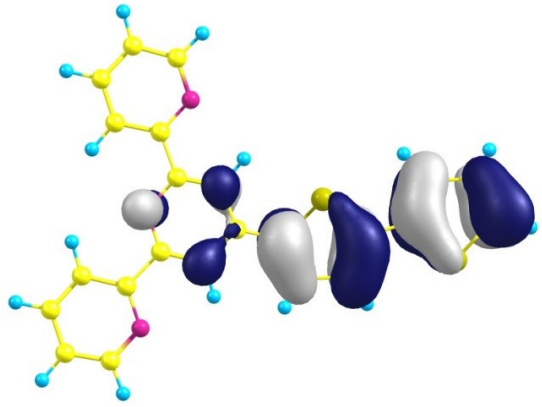
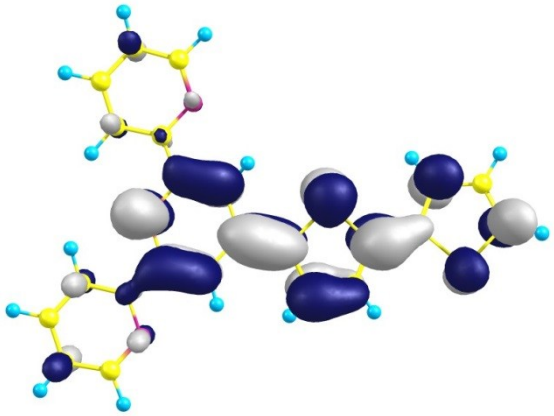
Solvent	Δf
Methanol	0.309
Acetonitryle	0.304
Acetone	0.285
N.N–dimethylformamide	0.275
Dimethyl sulfoxide	0.264
Dichloromethane	0.218
Ethyl acetate	0.201
Diethyl ether	0.160
Dipropyl ether	0.120
Cyclohexane	0.0

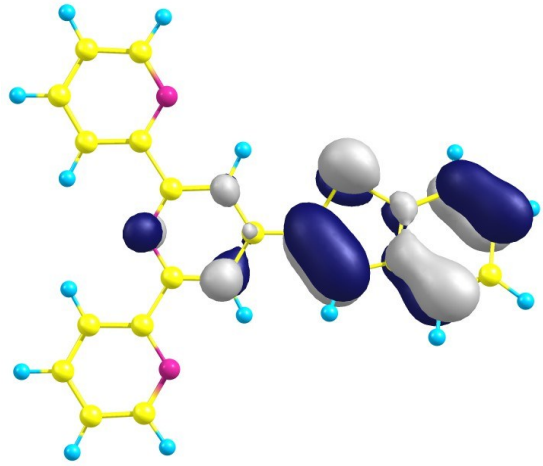
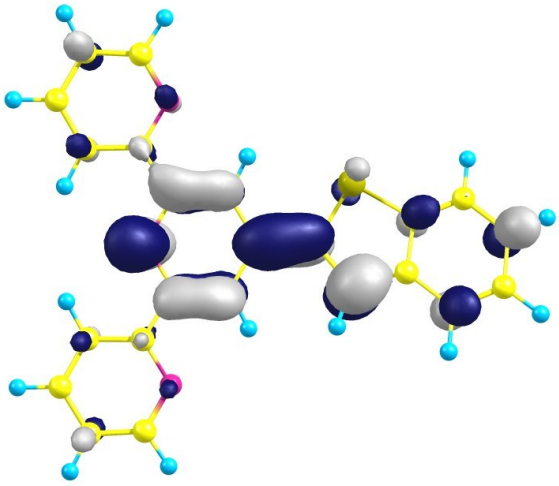
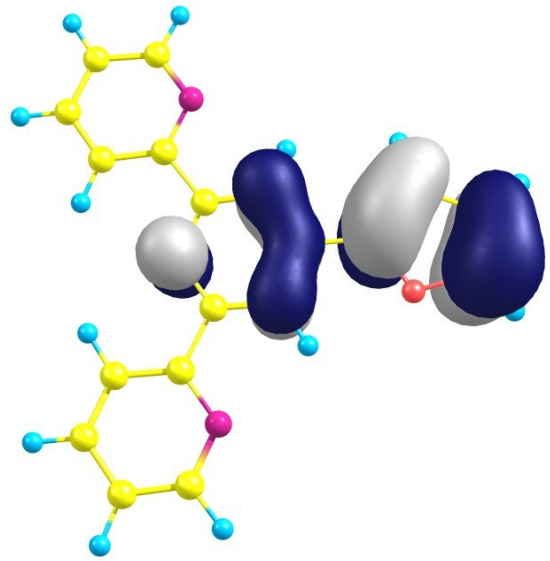
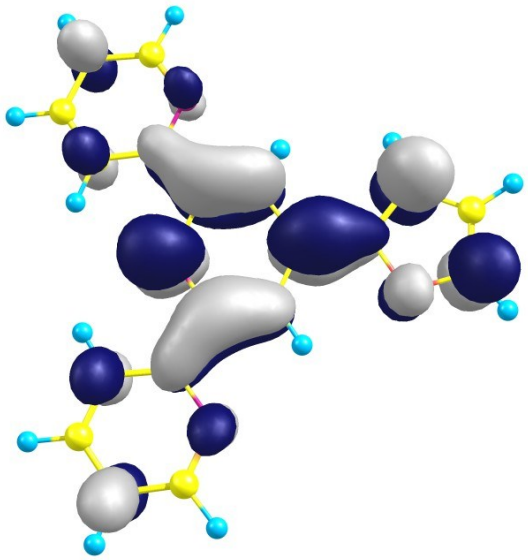
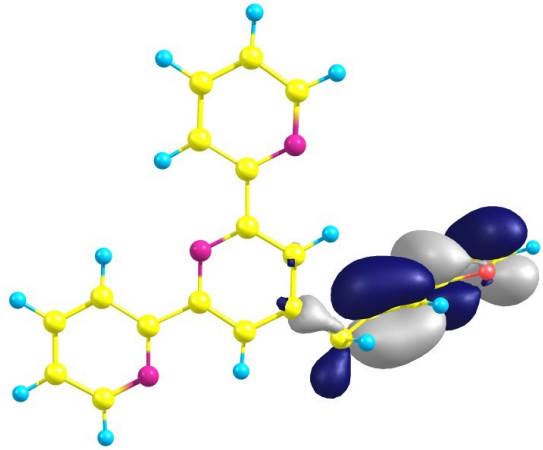
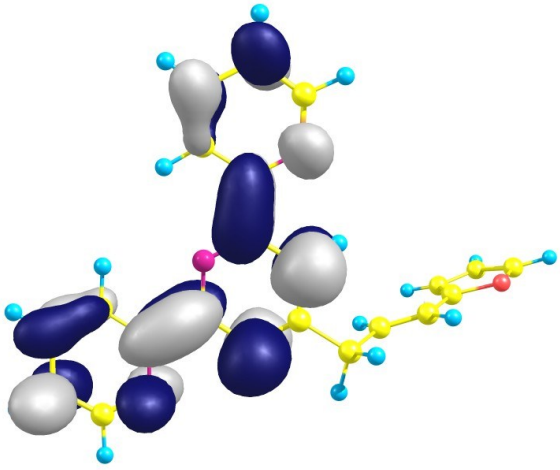
Figure S9. Frontier molecular orbitals of **1–R[1–16]** calculated at DFT/B3LYP level using the polarizable continuum model (MeCN).

Compound	**HOMO** (energy in eV)	LUMO
1–R[1]	 (–5.34 eV)	 (–1.80 eV)
1–R[2]	 (–6.07 eV)	 (–1.71 eV)
1–R[3]	 (–5.61 eV)	 (–1.60 eV)

1–R[4]	 (–6.43 eV)	 (–1.74 eV)
1–R[5]	 (–6.43 eV)	 (–1.73 eV)
1–R[6]	 (–6.43 eV)	 (–1.75 eV)

1–R[7]	 (–5.11 eV)	 (–1.52 eV)
1–R[8]	 (–6.46 eV)	 (–1.89 eV)
1–R[9]	 (–6.39 eV)	 (–1.87 eV)

1–R[10]	 (–5.65 eV)	 (–1.57 eV)
1–R[11]	 (–6.43 eV)	 (–1.83 eV)
1–R[12]	 (–5.64 eV)	 (–2.04 eV)

1–R[13]	 (–6.07 eV)	 (–1. 98 eV)
1–R[14]	 (–6.15 eV)	 (–1.77 eV)
1–R[15]	 (–5.67 eV)	 (–1.57 eV)

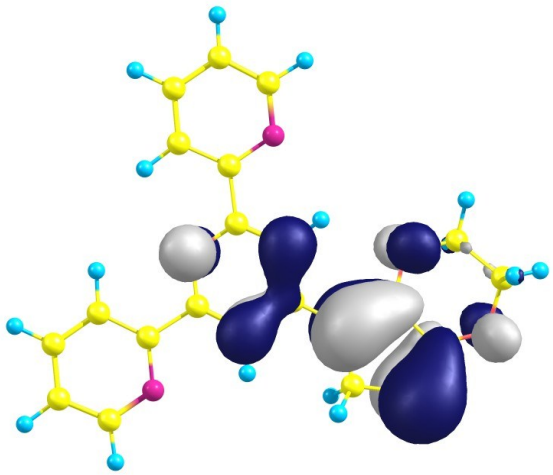
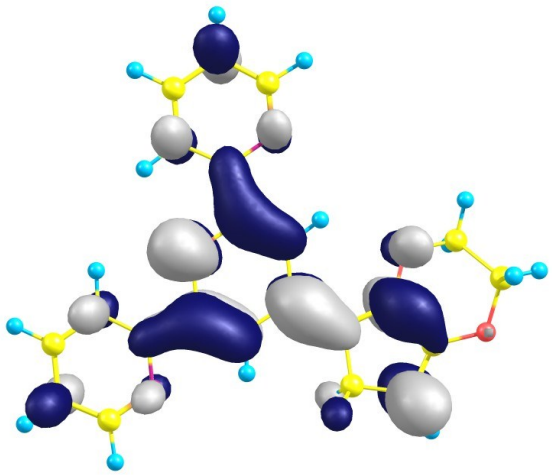
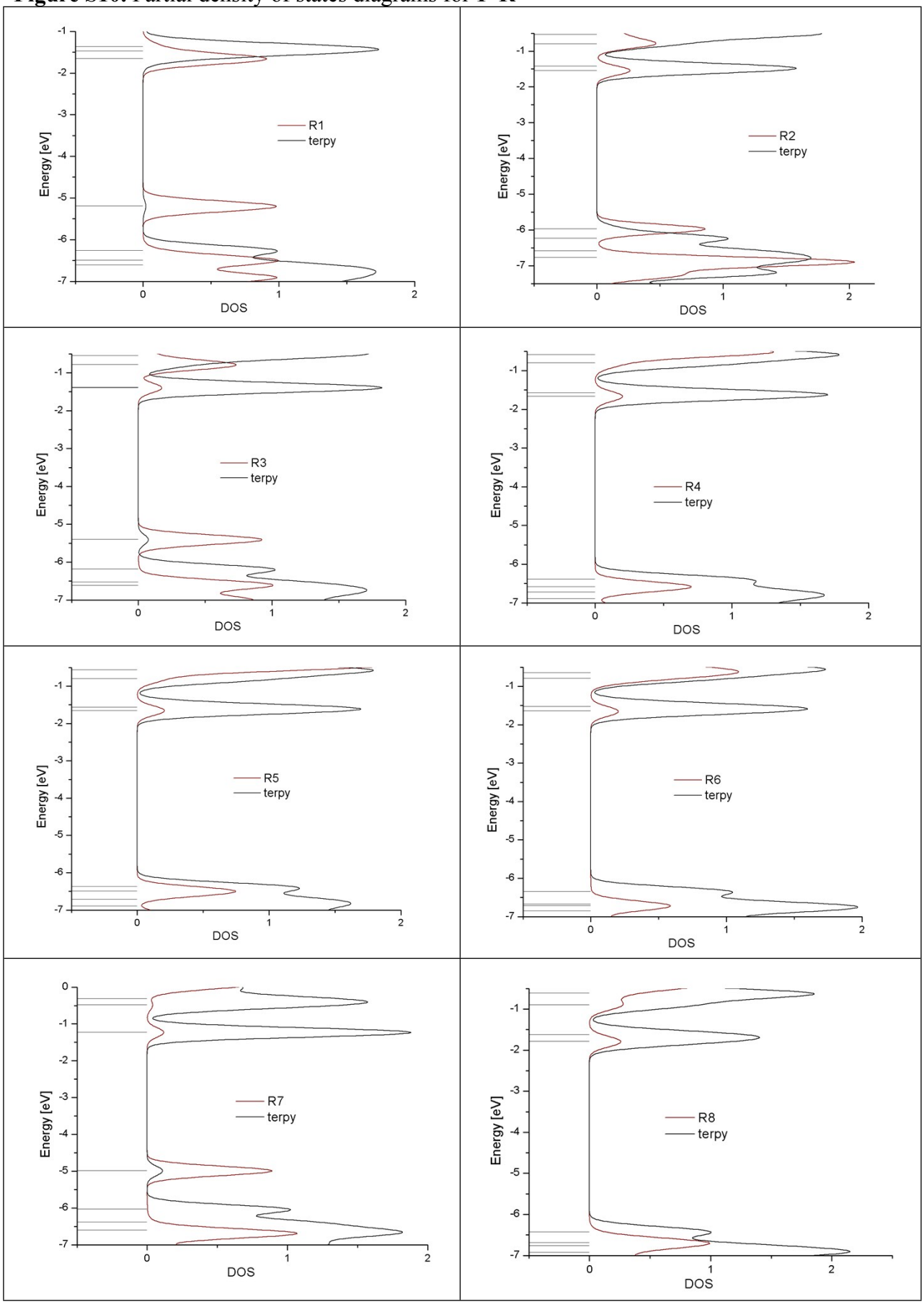
1–R[16]	 (–5.53 eV)	 (–1.69 eV)

Figure S10. Partial density of states diagrams for **1–R**[1–16]



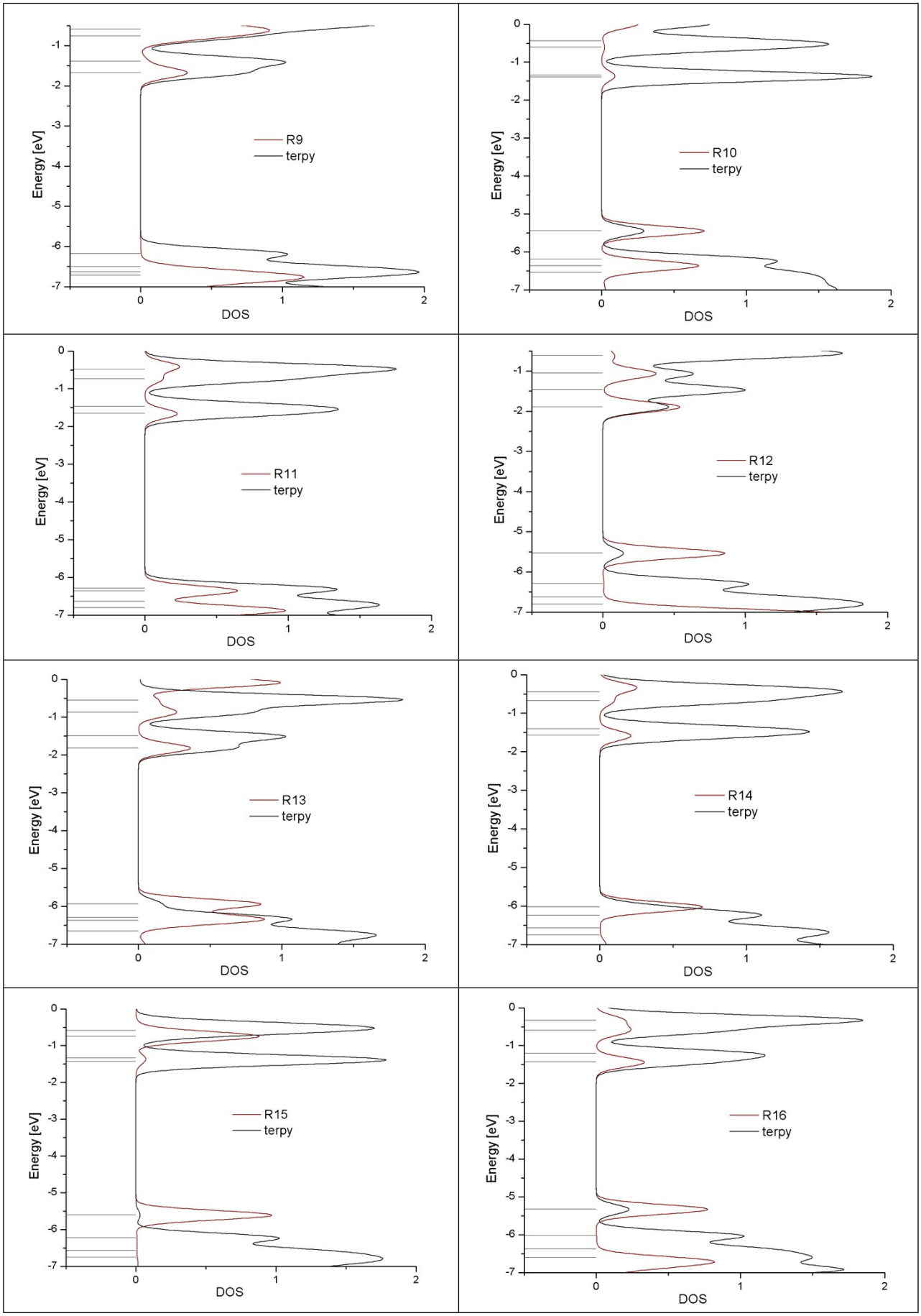
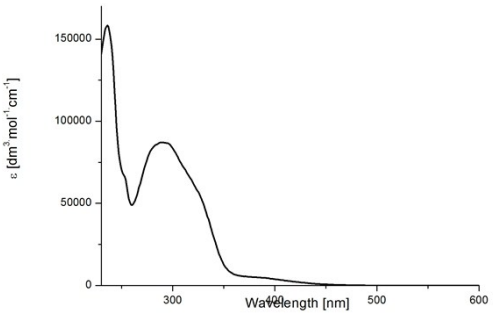
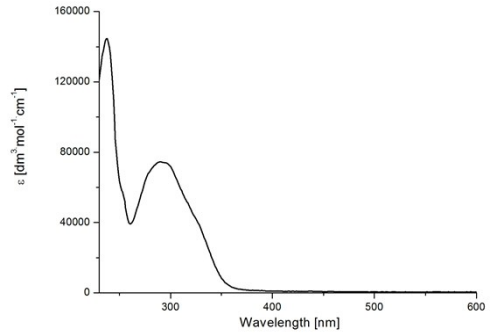
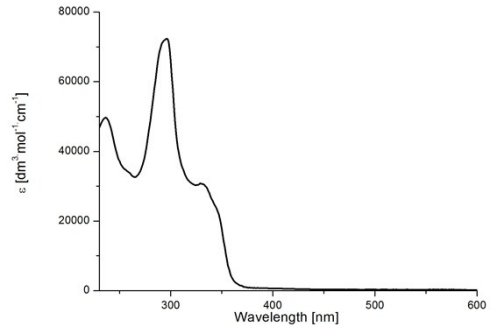
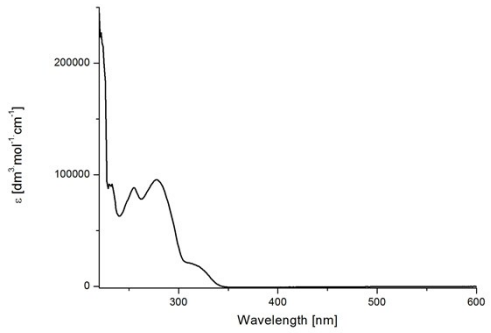
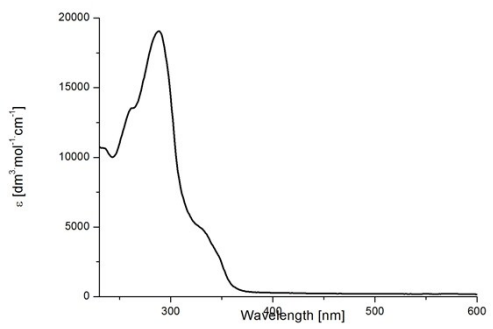
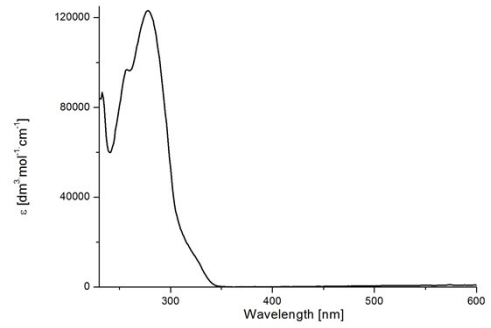
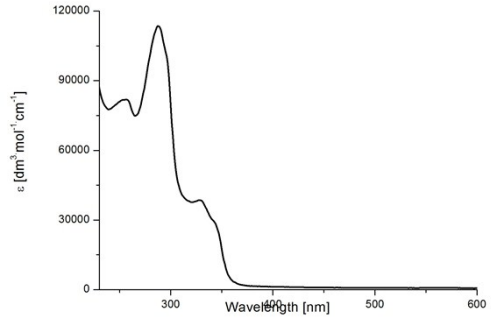
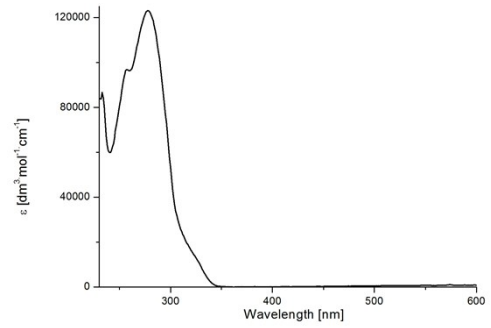

Energy [eV]
DOS
R9
terpy
R10
terpy
R11
terpy
R12
terpy
R13
terpy
R14
terpy
R15
terpy
R16
terpy

Figure S11. Electronic absorption spectra of compounds **1–R[3–6]**, **1–R[8–9]**, **1–R[11]**, **1–R[13–14]**.

Compound	CH_3CN	CH_2Cl_2
1–R[3]		
1–R[4]		
1–R[5]		
1–R[6]		

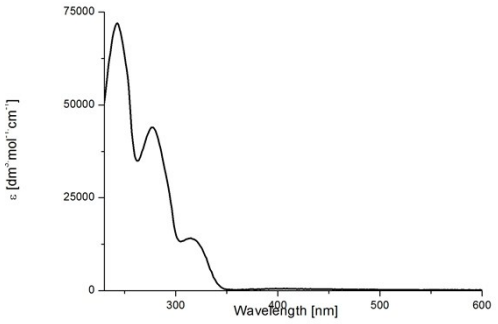
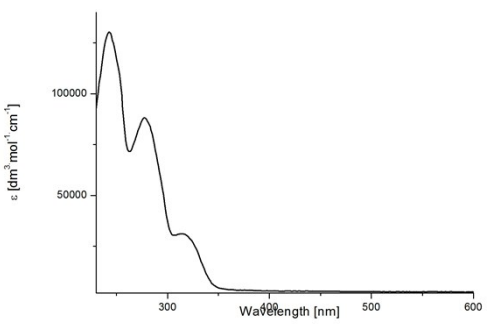
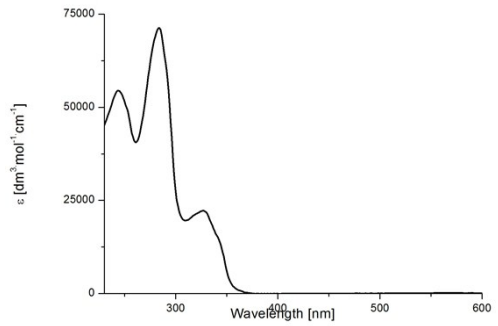
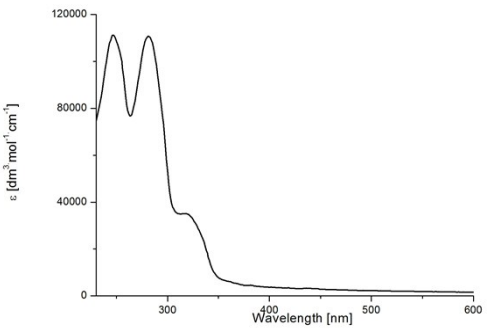
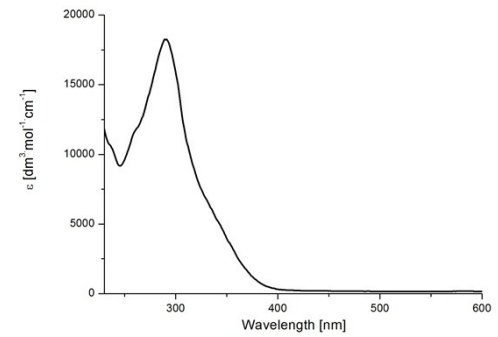
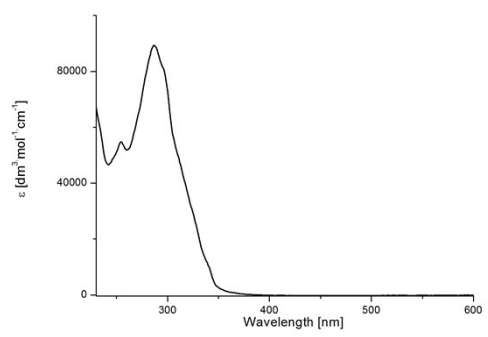
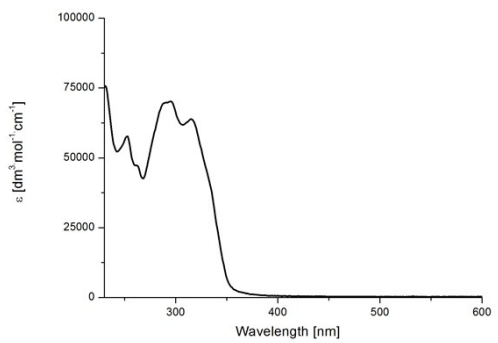
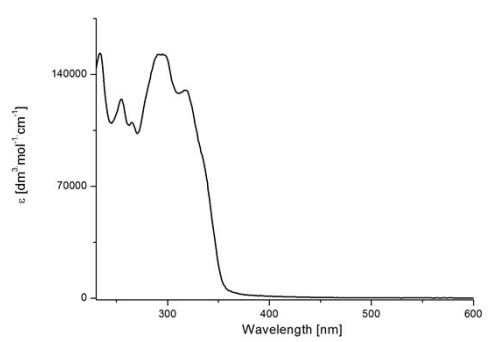
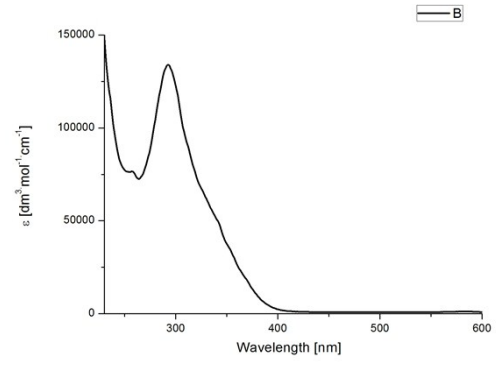
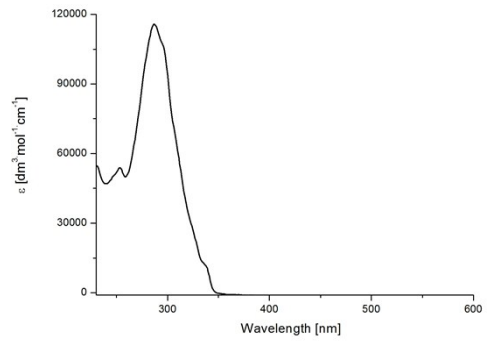
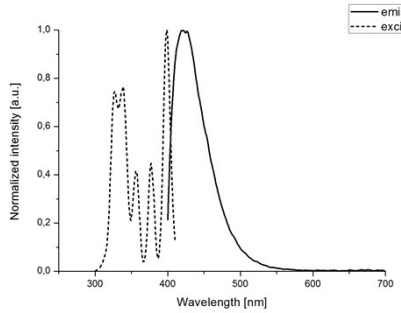
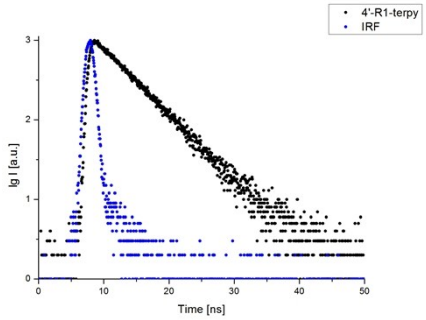
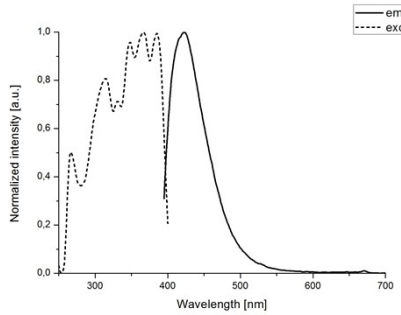
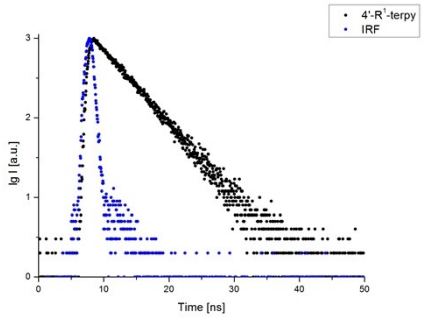
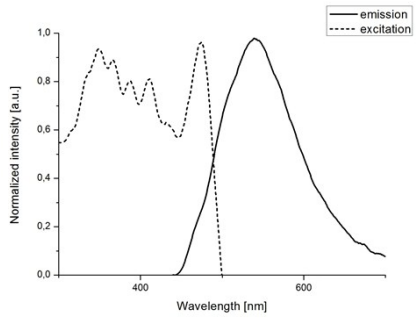
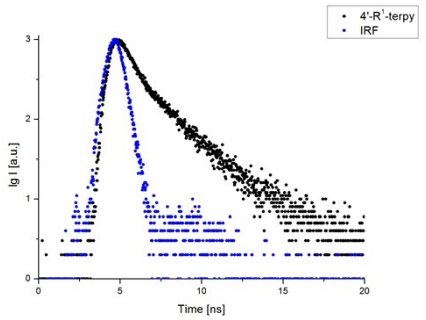
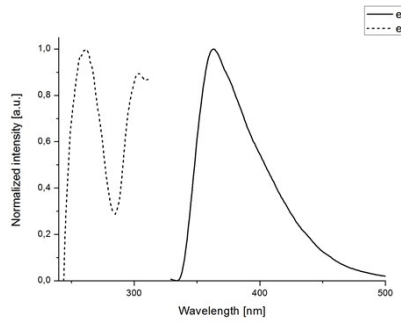
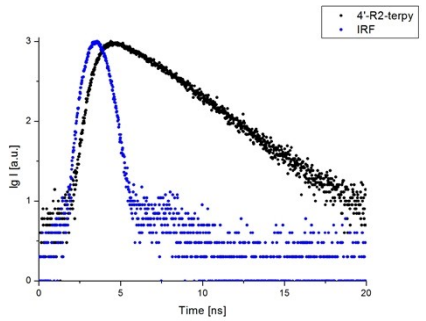
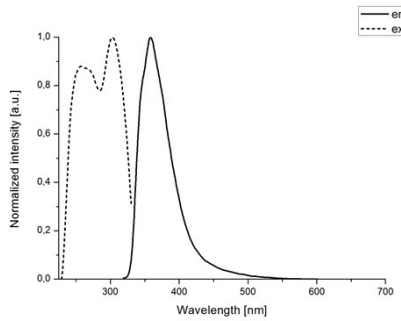
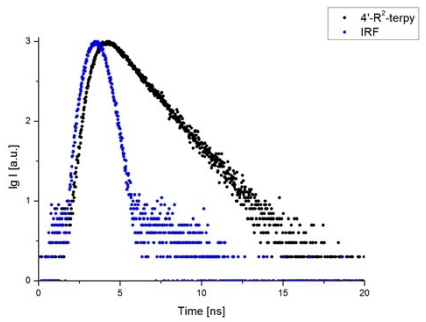
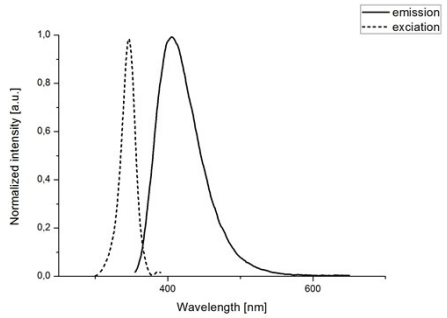
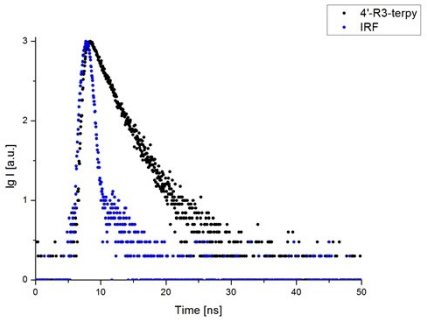
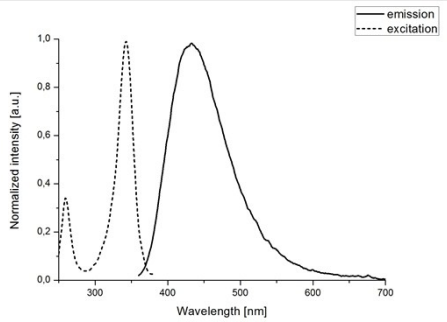
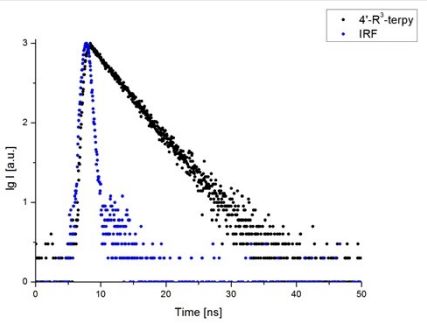
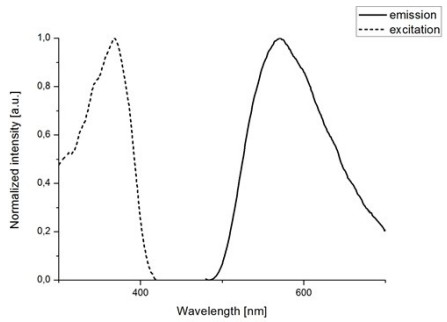
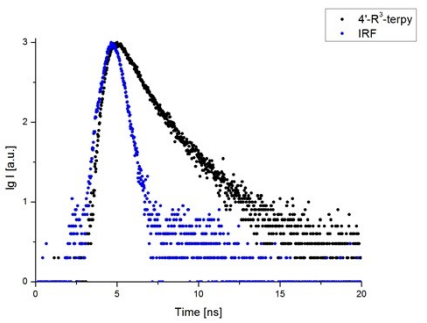
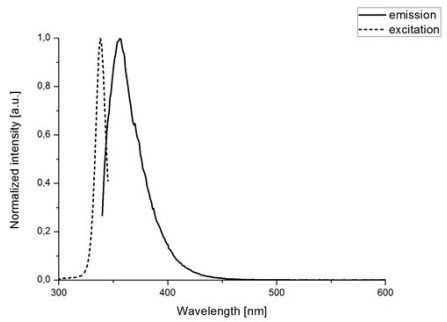
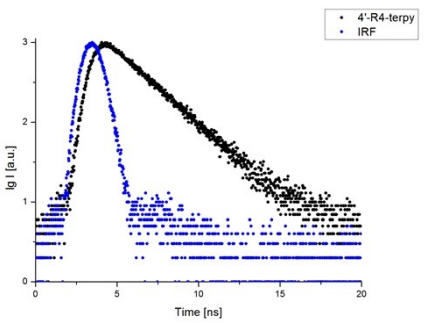
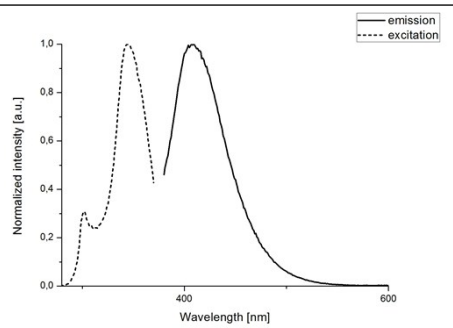
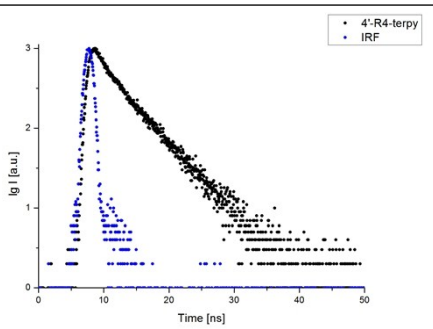
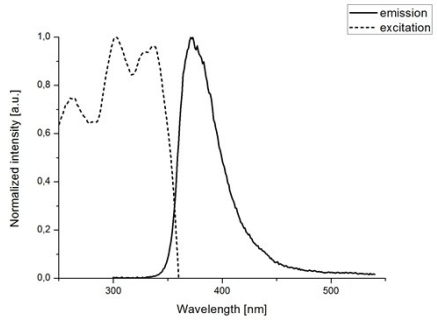
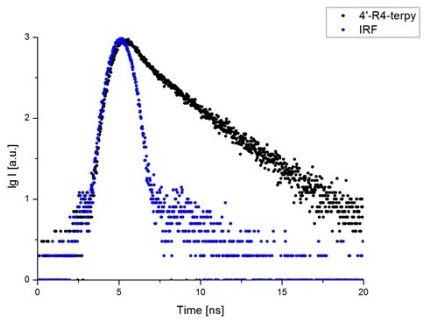
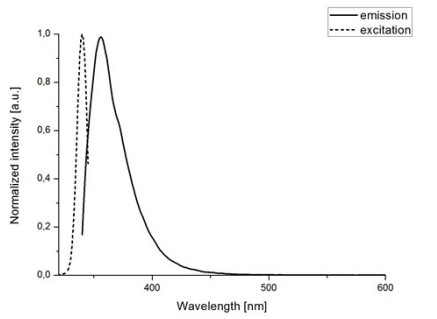
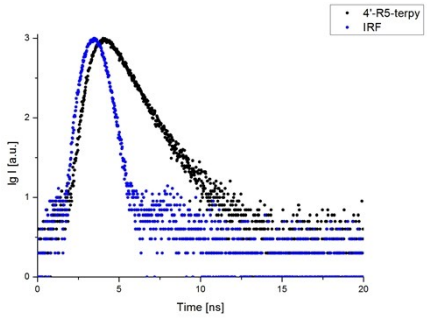
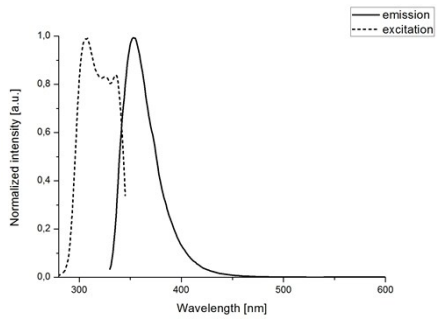
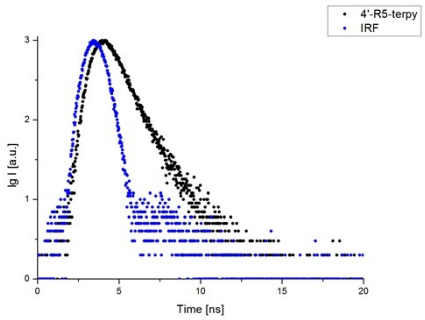
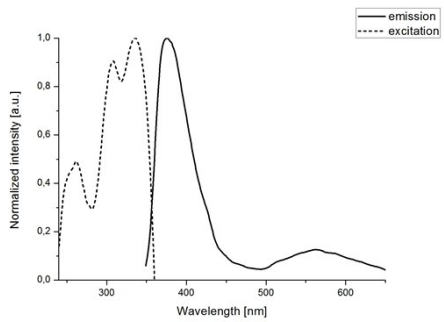
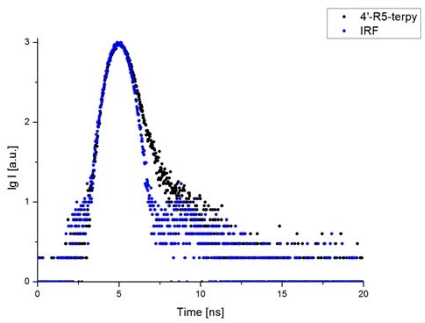
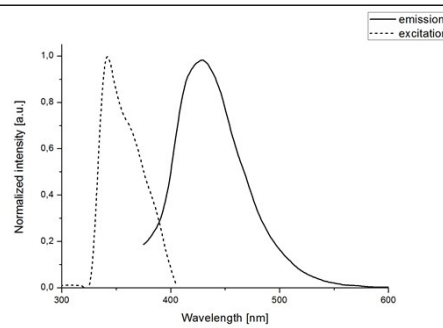
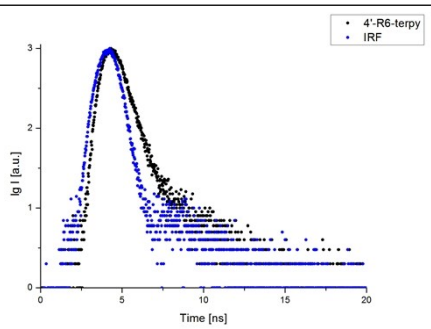
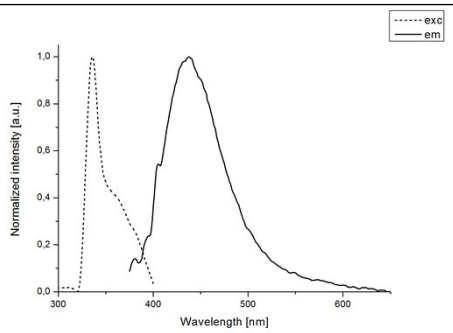
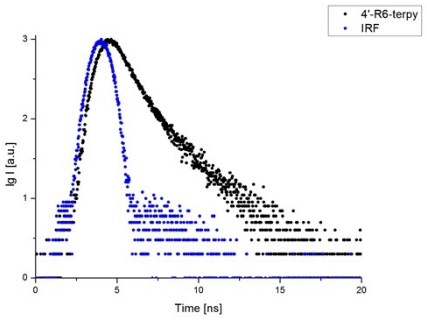
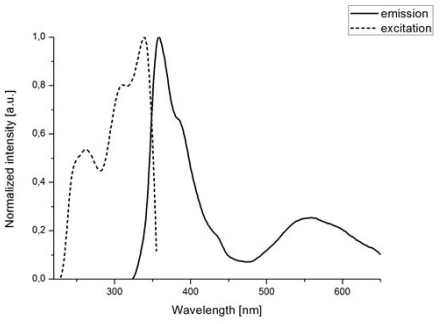
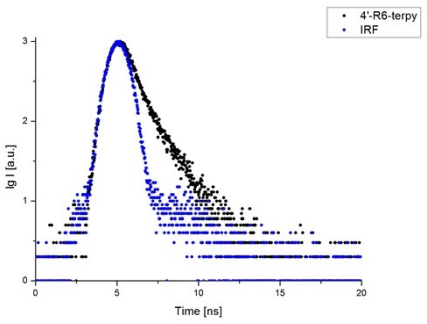
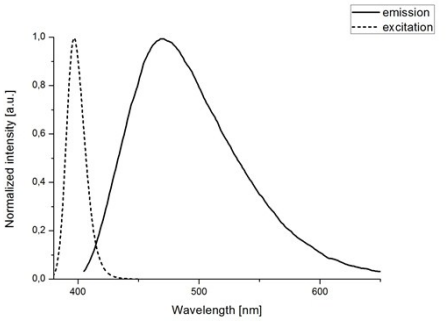
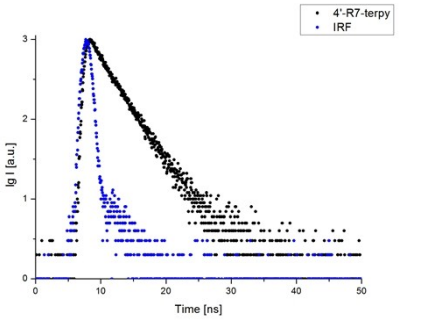
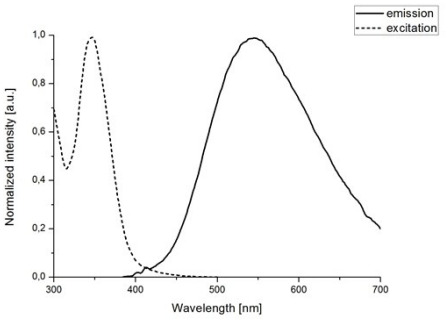
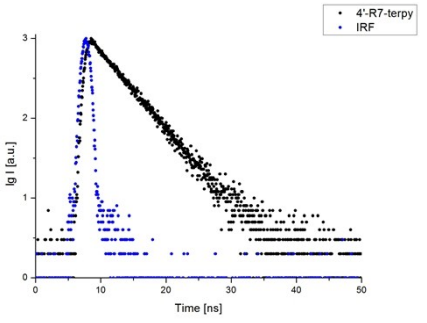
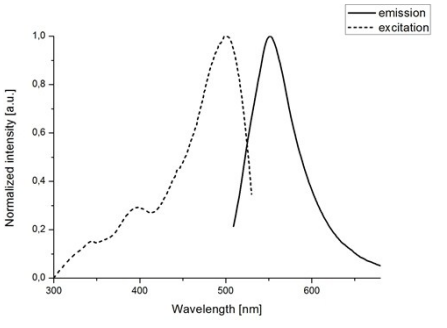
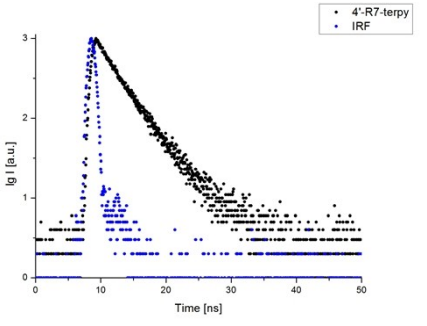
1–R[8]		
1–R[9]		
1–R[11]		
1–R[13]		
1–R[14]		

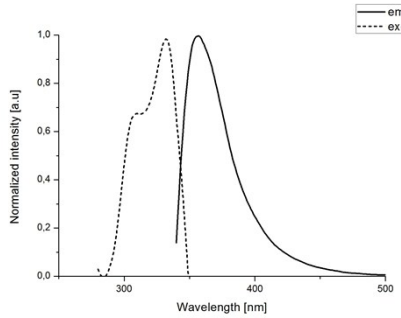
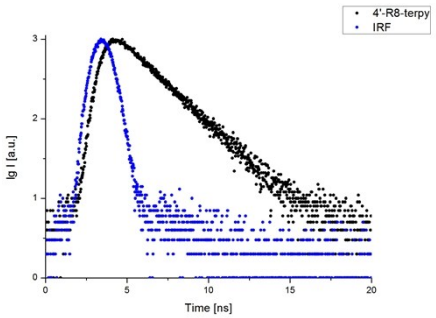
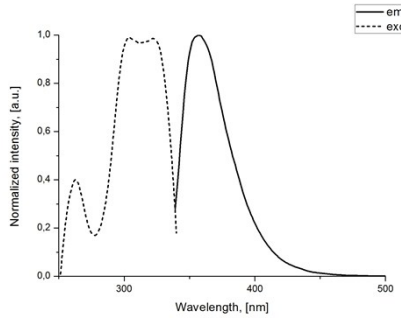
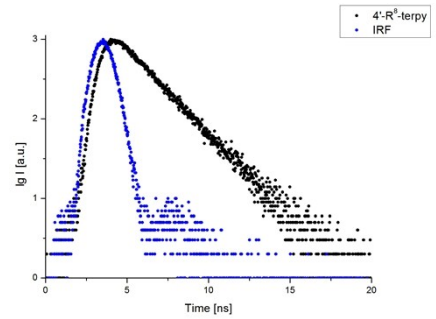
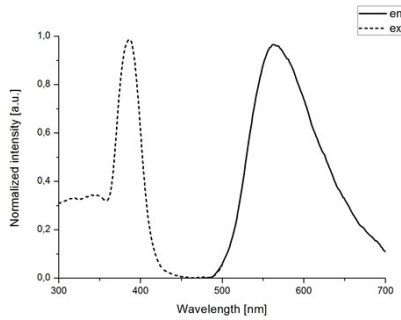
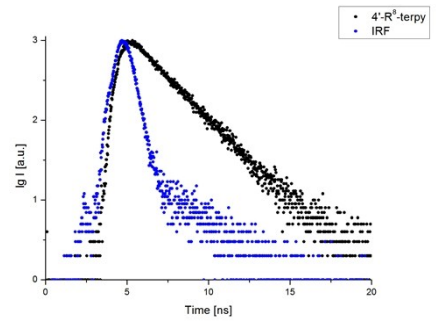
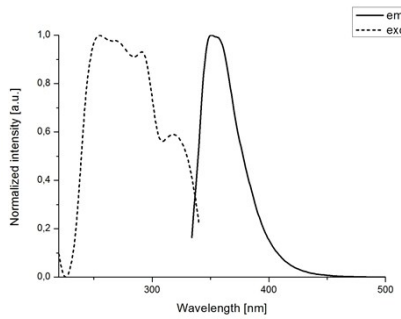
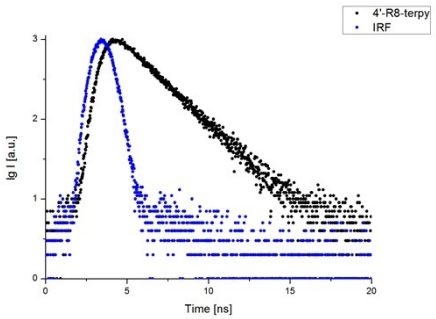
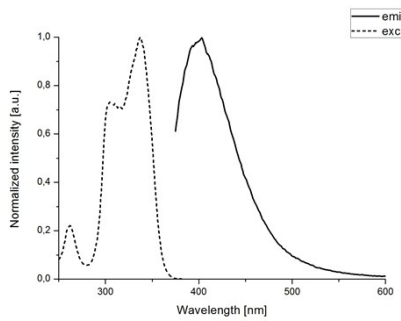
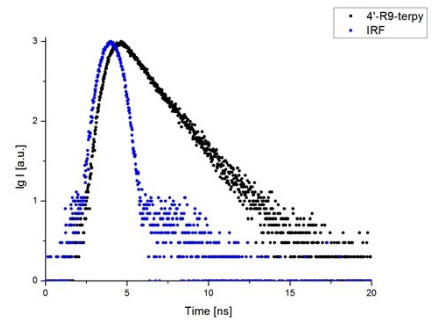
Figure S12. Excitation and emission spectra of compounds **1–R[1–16]**.

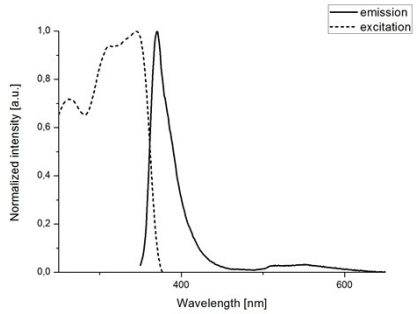
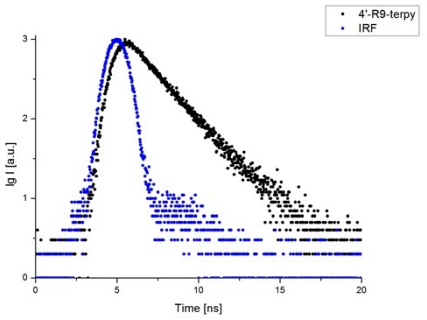
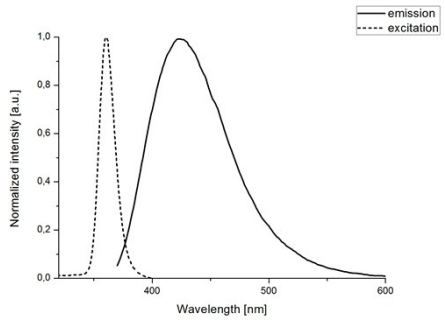
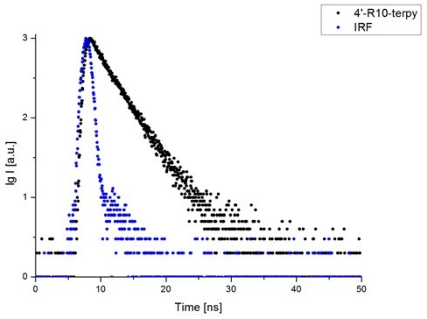
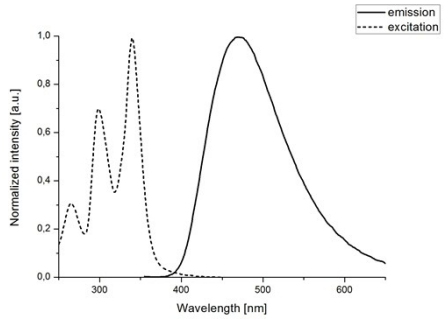
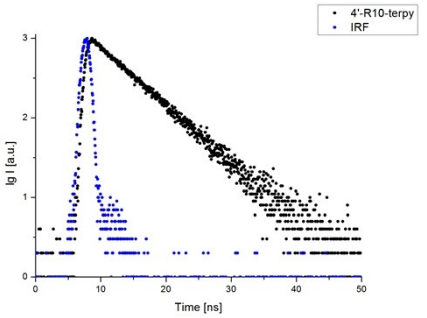
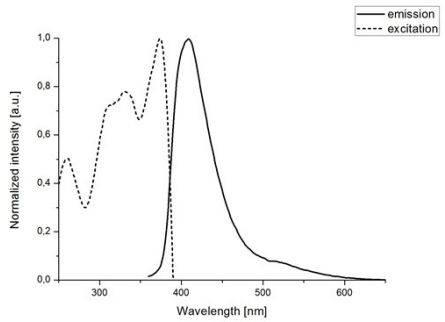
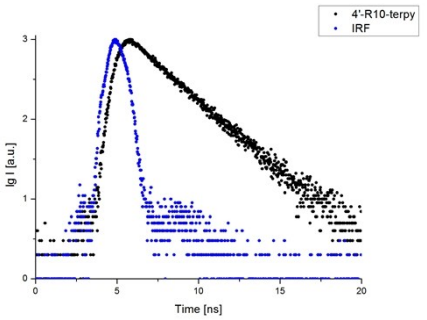
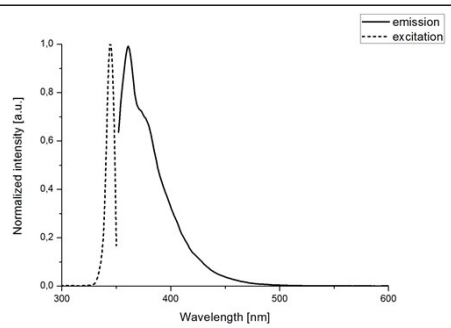
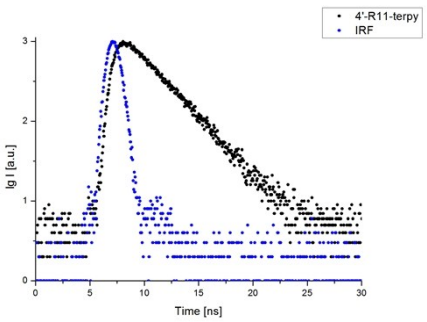
Medium	Excitation and emission spectra	PL lifetime curve
1–R[1]		
CH_2Cl_2		
MeCN		
Solid		
1–R[2]		
CH_2Cl_2		
MeCN		
Solid		
1–R[3]		

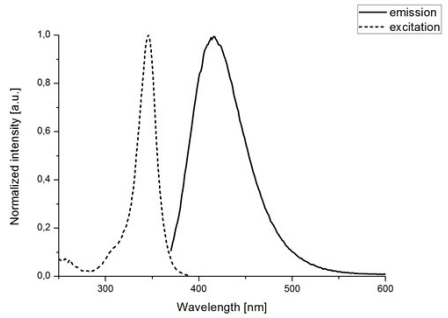
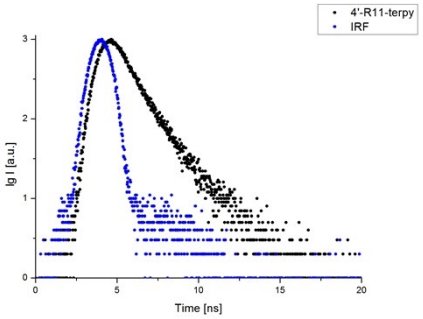
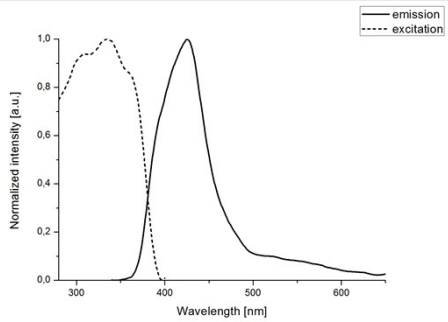
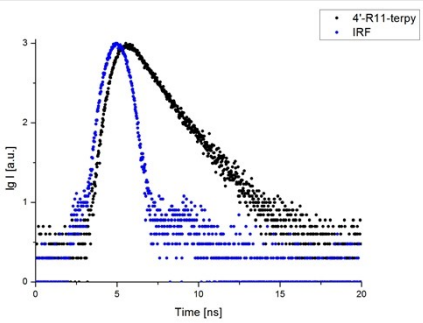
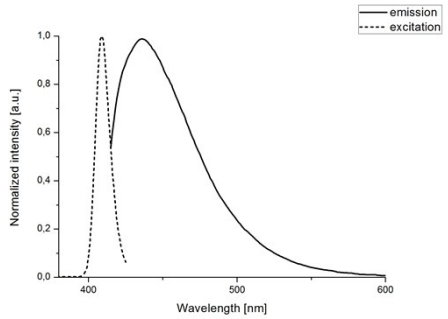
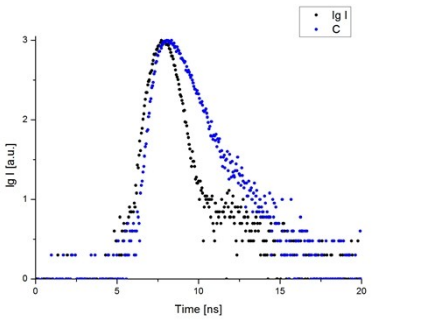
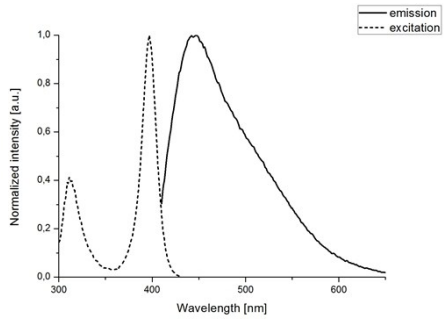
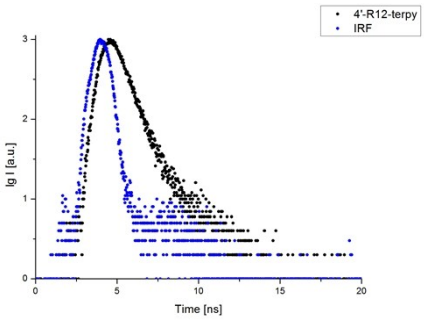
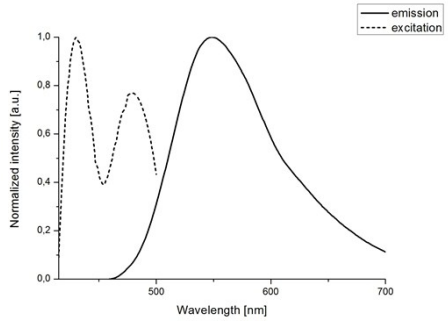
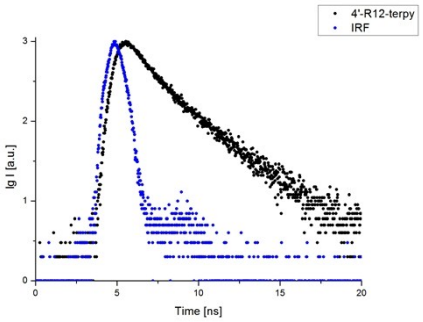
CH_2Cl_2		
MeCN		
Solid		
1–R⁴		
CH_2Cl_2		
MeCN		

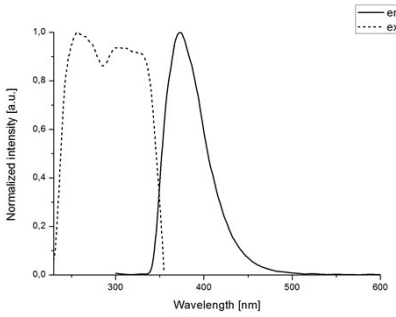
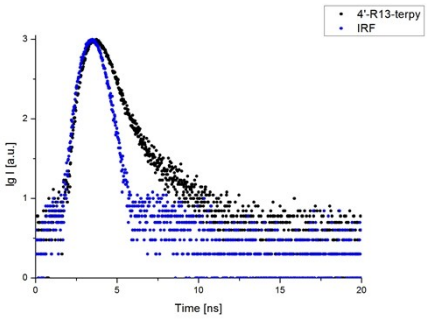
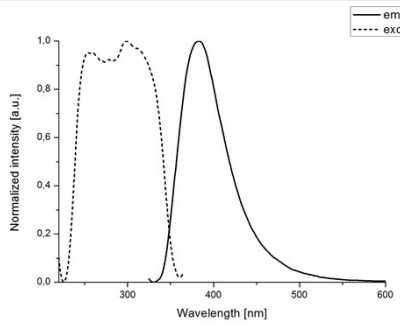
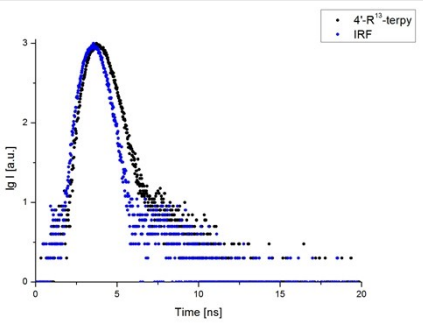
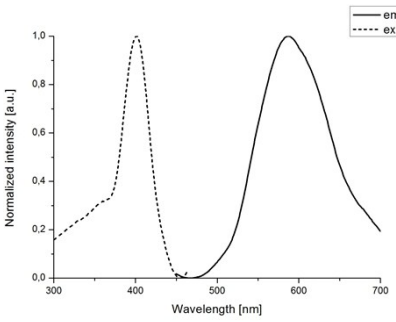
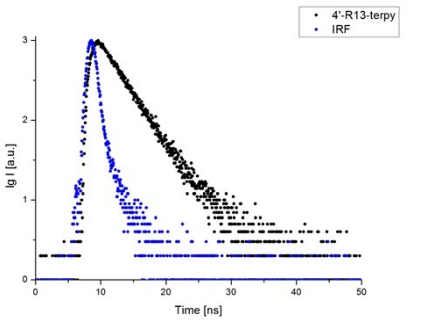
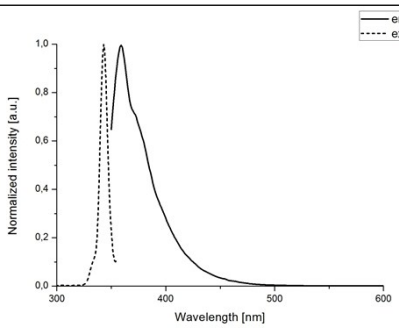
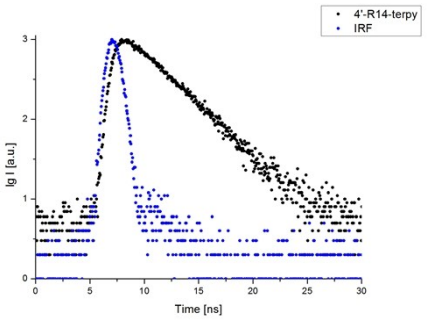
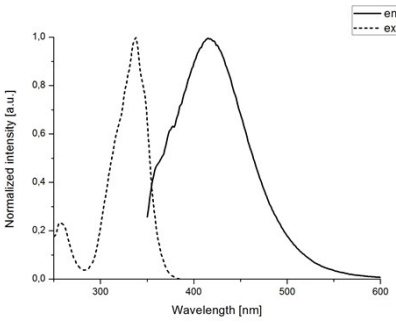
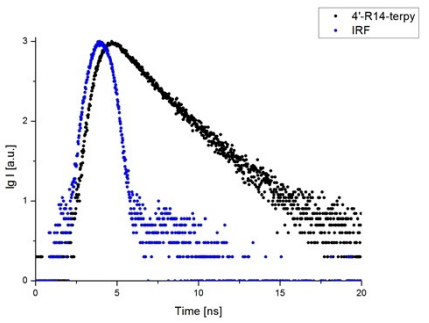
Solid		
1–R^5		
CH_2Cl_2		
MeCN		
Solid		
1–R^6		
CH_2Cl_2		

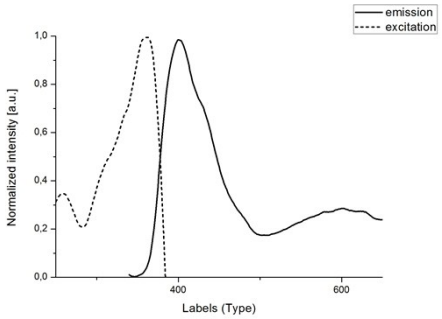
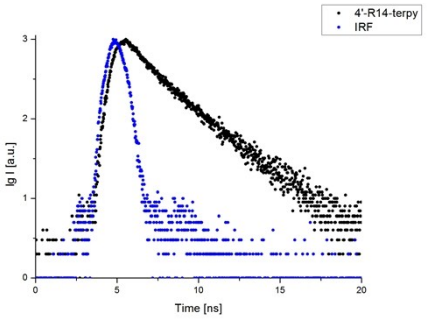
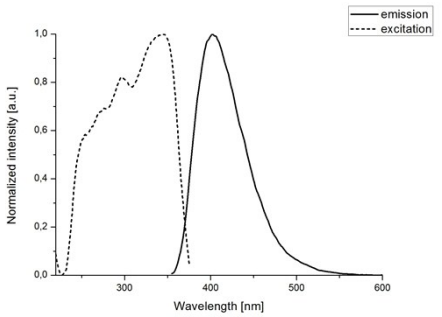
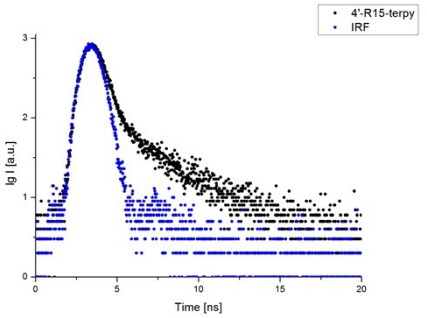
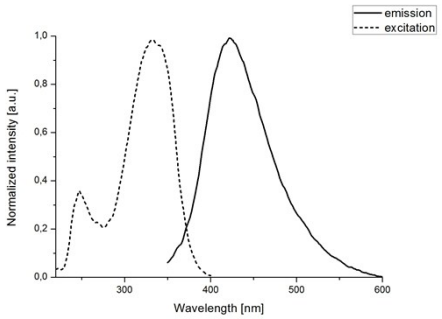
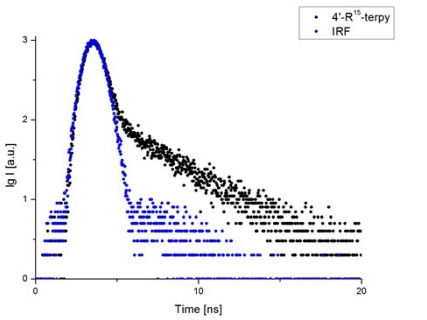
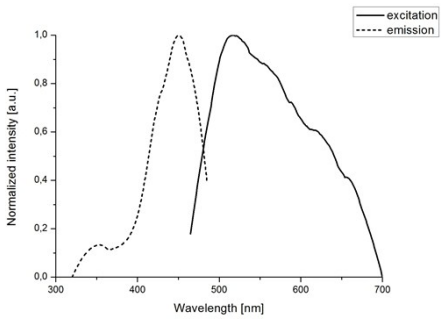
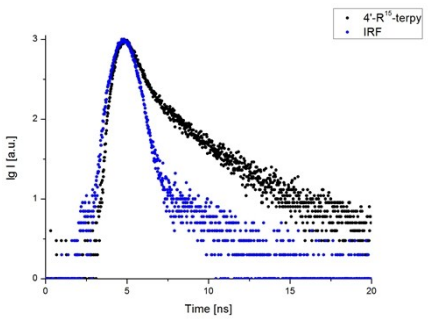
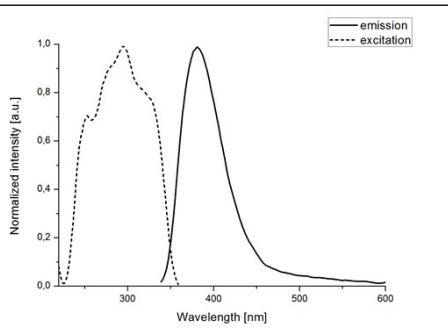
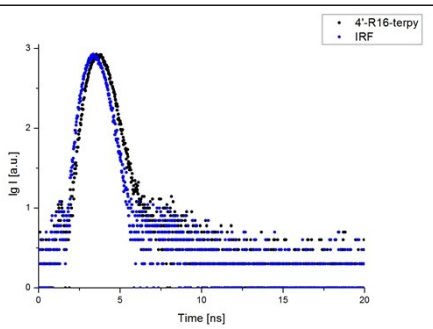
MeCN		
Solid		
1–R⁷		
CH_2Cl_2		
MeCN		
Solid		
1–R⁸		

CH_2Cl_2		
MeCN		
Solid		
	1–R^9	
CH_2Cl_2		
MeCN		

Solid		
1–R[10]		
CH_2Cl_2		
MeCN		
Solid		
1–R[11]		
CH_2Cl_2		

MeCN		
Solid		
1–R[12]		
CH_2Cl_2		
MeCN		
Solid		
1–R[13]		

CH_2Cl_2		
MeCN		
Solid		
	1–R^{14}	
CH_2Cl_2		
MeCN		

Solid		
1–R^{15}		
CH_2Cl_2		
MeCN		
Solid		
1–R^{16}		
CH_2Cl_2		

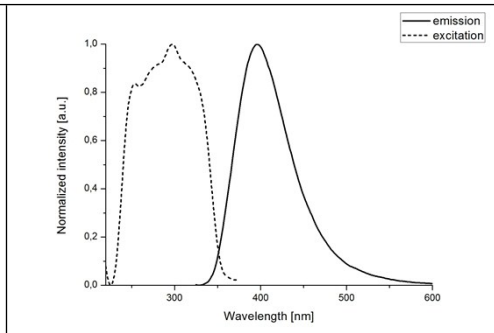
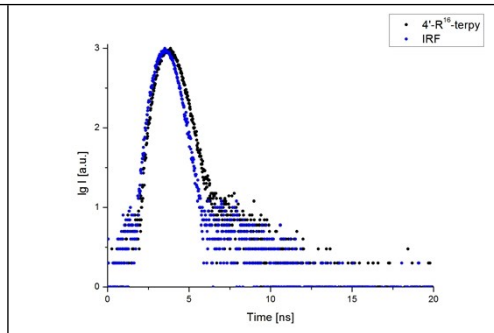
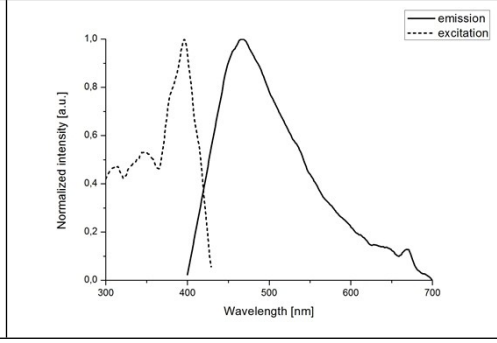
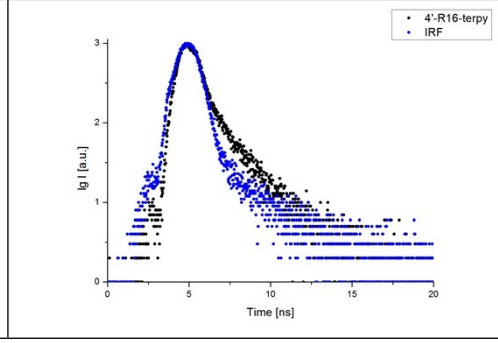
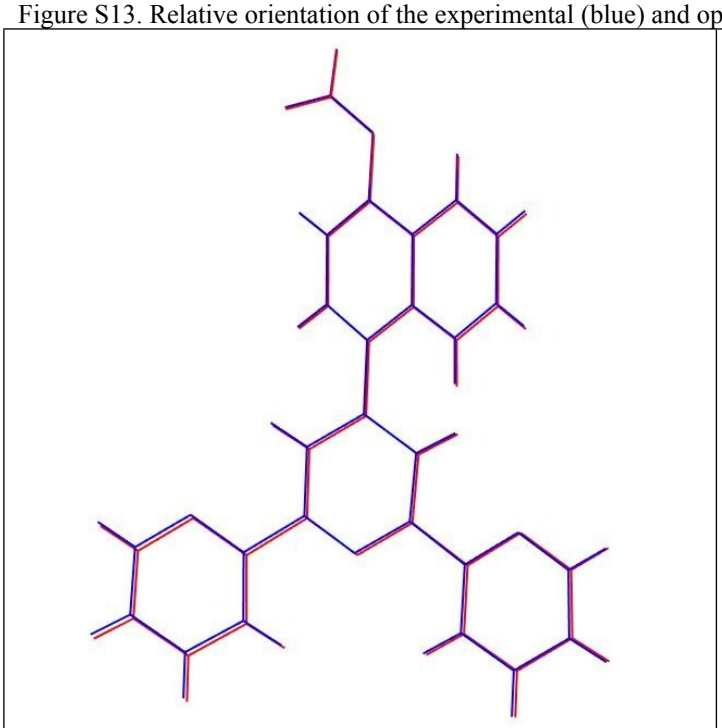
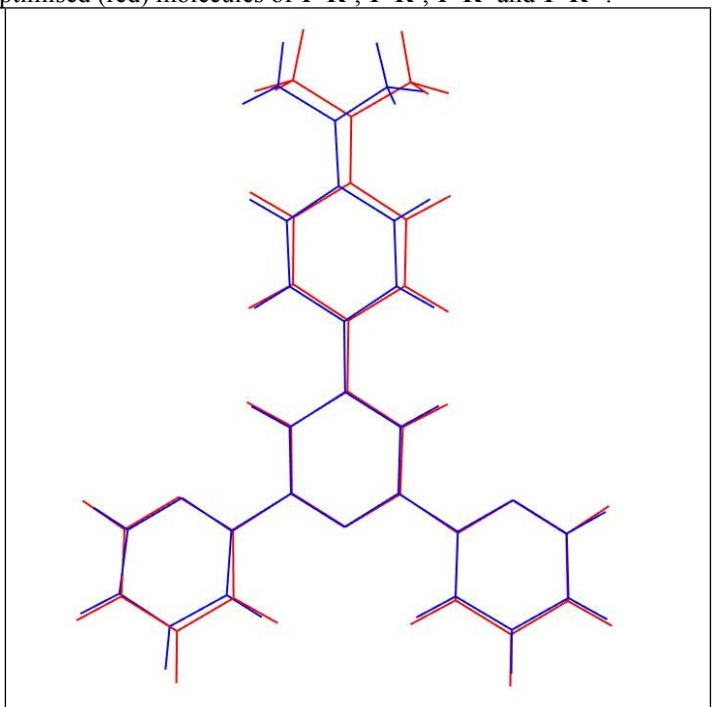
MeCN		
Solid		

Figure S13. Relative orientation of the experimental (blue) and optimised (red) molecules of **1–R^{3}**, **1–R^{7}**, **1–R^{8}** and **1–R^{14}**.

	
1–R^{3}	**1–R^{7}**

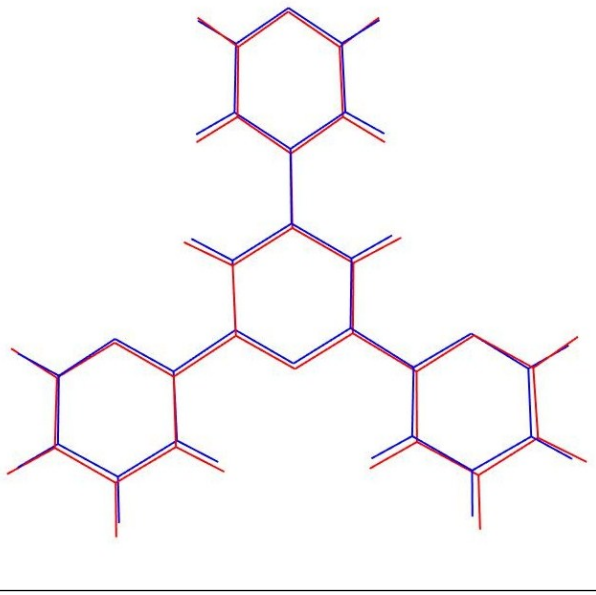
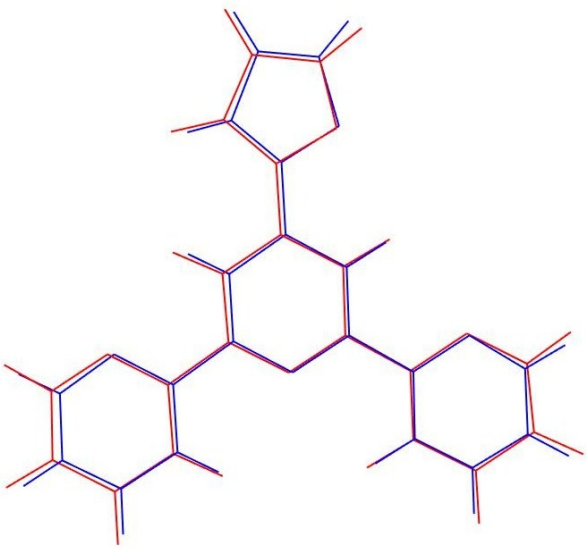
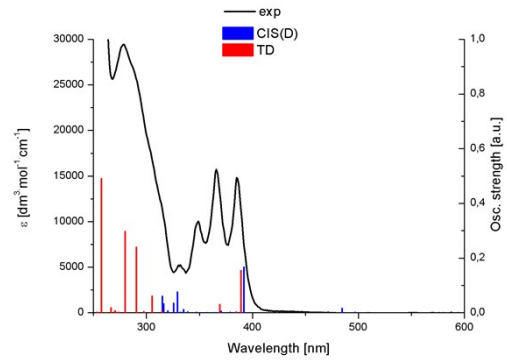
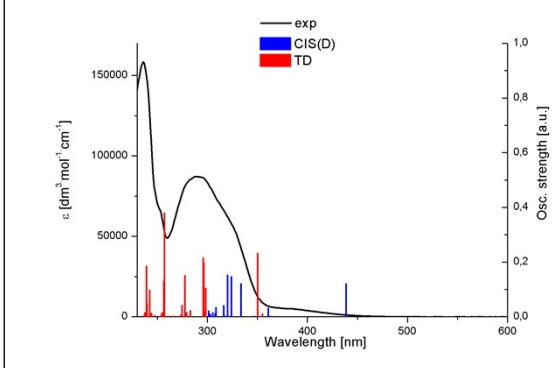
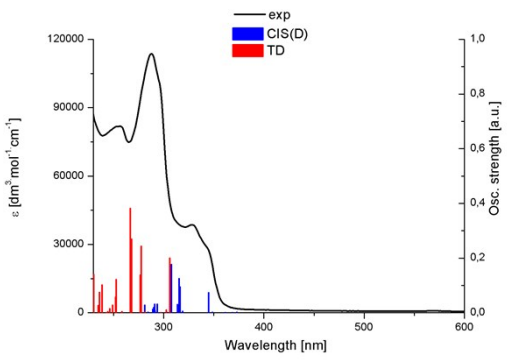
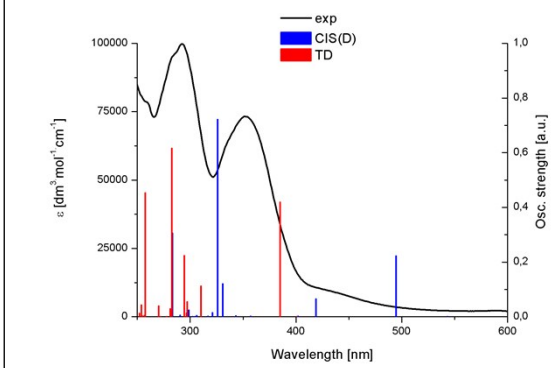
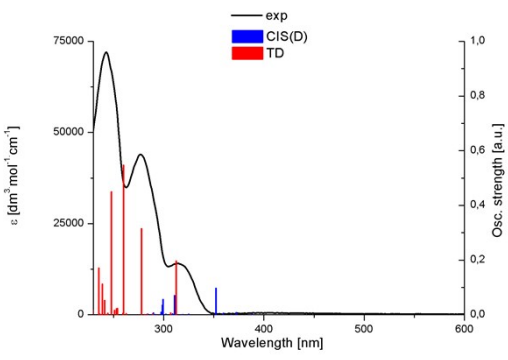
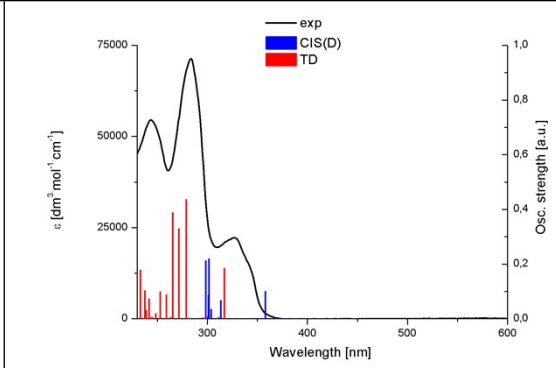
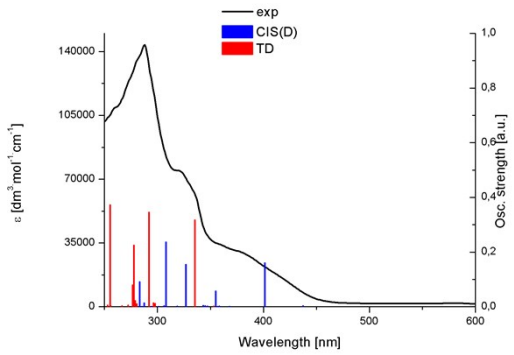
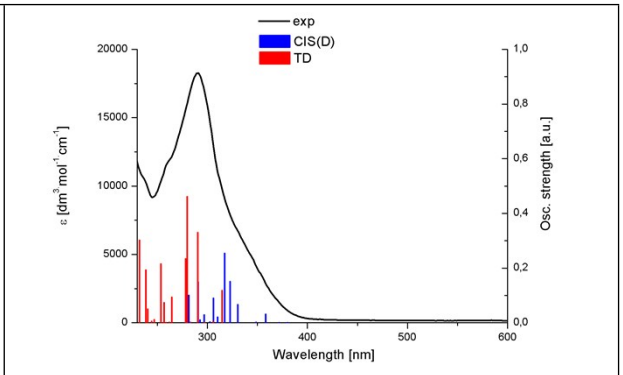
	
1–R[8]	**1–R[14]**

Figure S14. Experimental and calculated with CIS(D) and TD-DFT method absorption spectra

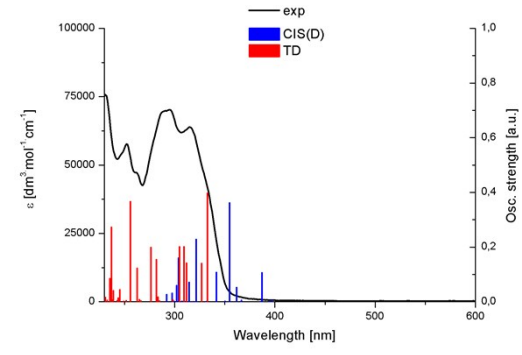
	
1–R[1]	1–R[3]
	
1–R[6]	1–R[7]
	
1–R[8]	1–R[9]



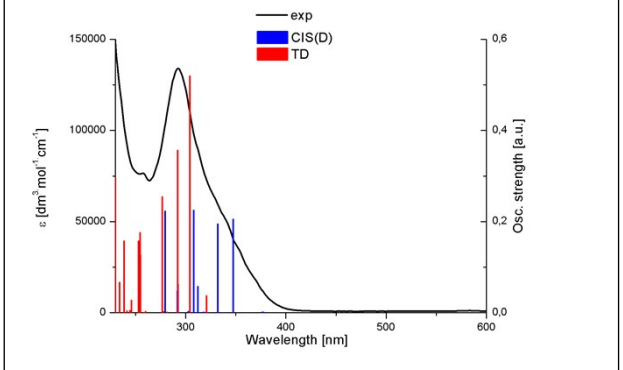
1–R[10]



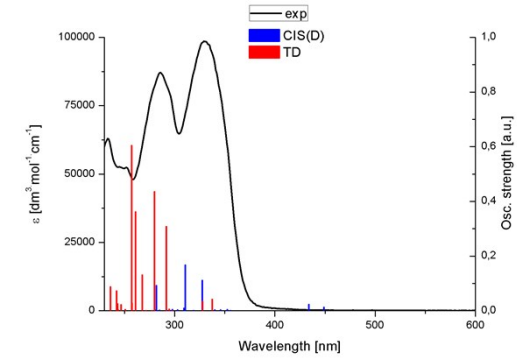
1–R[11]



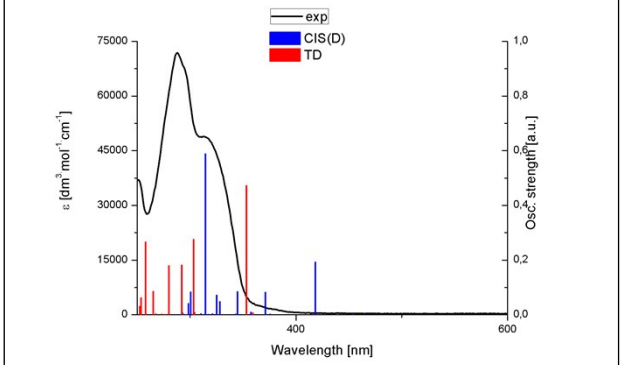
1–R[13]



1–R[14]



1–R[15]



1–R[16]