Supplementary file

Mechanosynthesis of polyureas and studies of their response to anions

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Experimental part

General method for the synthesis of Polyureas PUs.

For the synthesis of polyurea, isomeric 4,4-(1), 3,3(2) and 2,2(3) - diaminobiphenyls with 1.5 eq of triphosgene in 7 eq. Potassium carbonate as catalyst with 4 balls for 4 hours at a speed rotation of 500 rpm. after the reaction completed was washed by 10% aqueous solution of HCl, water, EtOH and acetone.

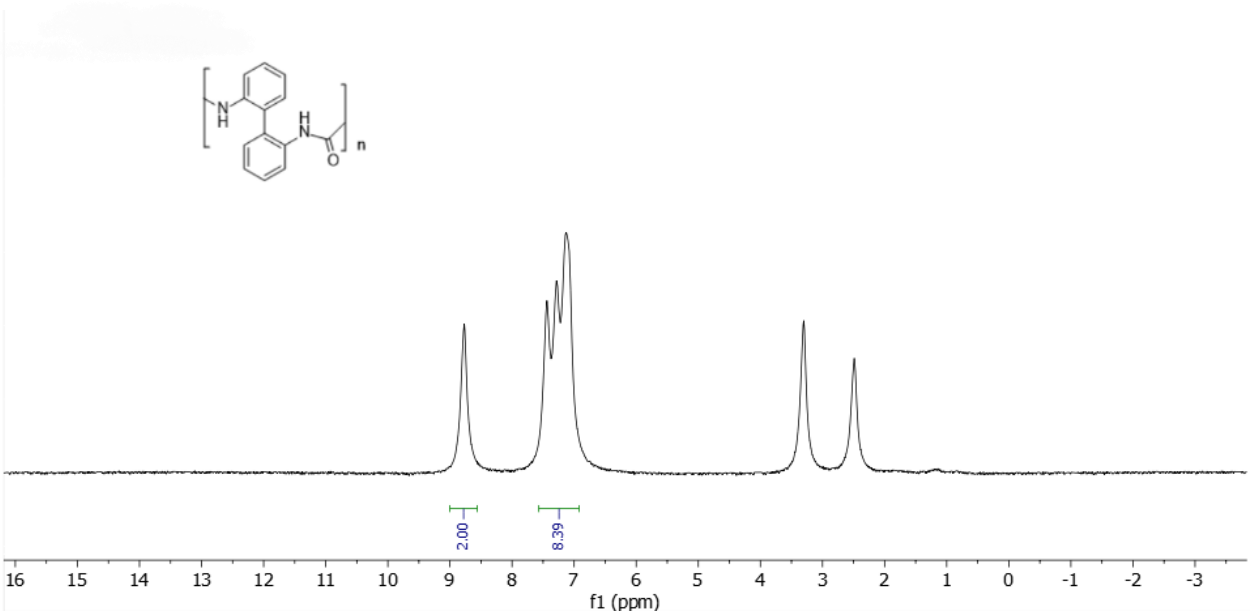


Figure S1. ^{1}H NMR spectrum of the (4) in DMSO-d_6 at r.t

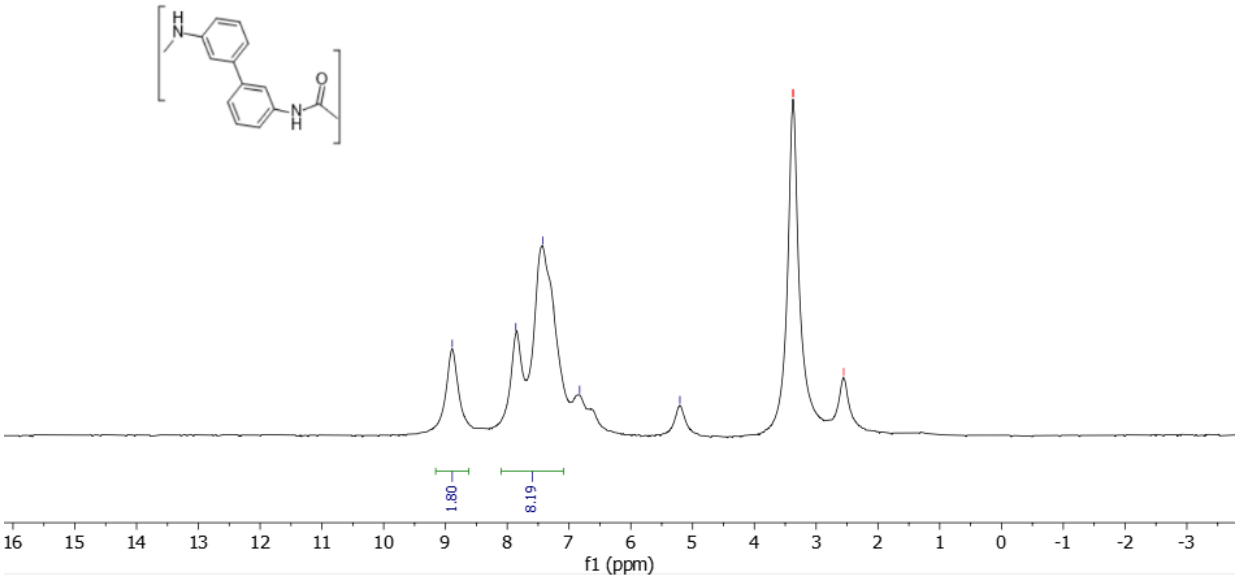


Figure S2. ^{1}H NMR spectrum of the (5) in DMSO-d_6 at r.t

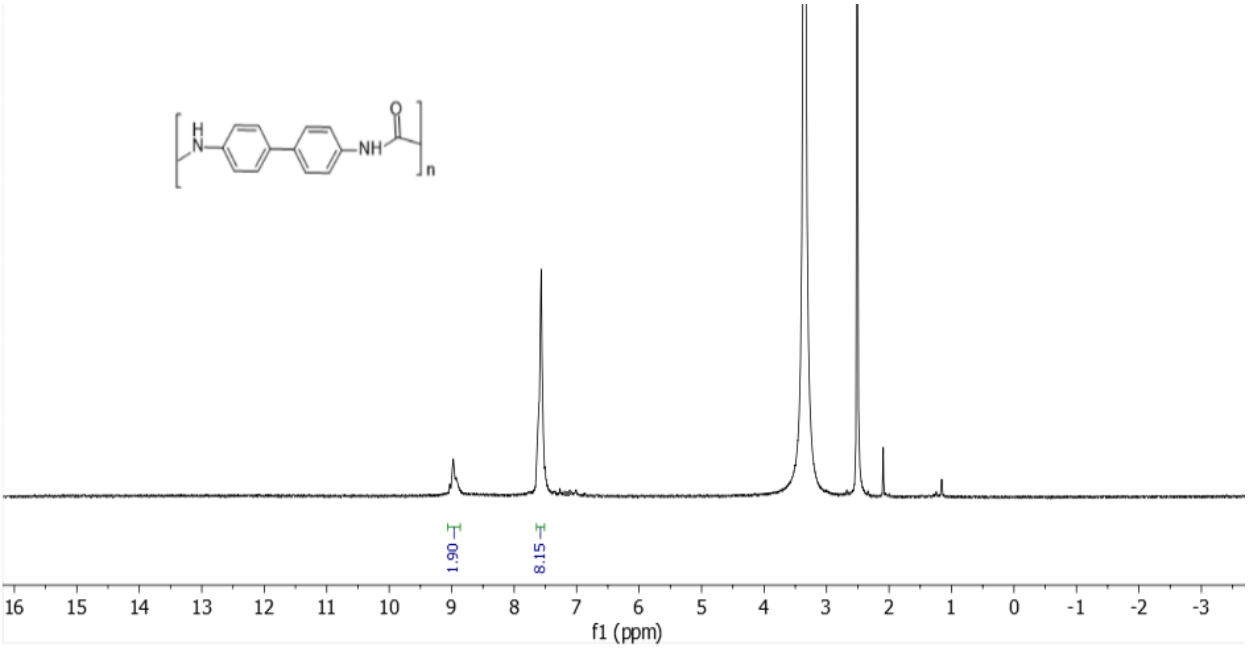


Figure S3. 1H NMR spectrum of the (6) in DMSO-d_6 at r.t

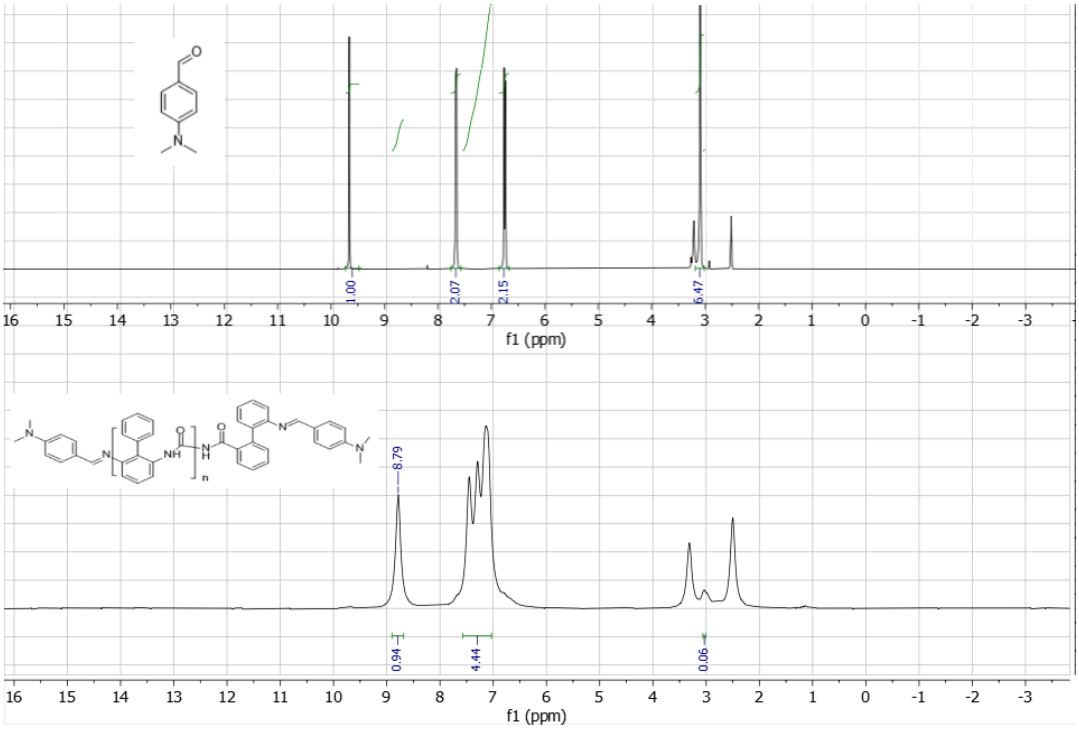


Figure S4. ^{1}H NMR spectrum of the (7) in DMSO-d_6 at r.t with N,N-dimethylamine moiety for determination molecular weight (Mn) of PUs .

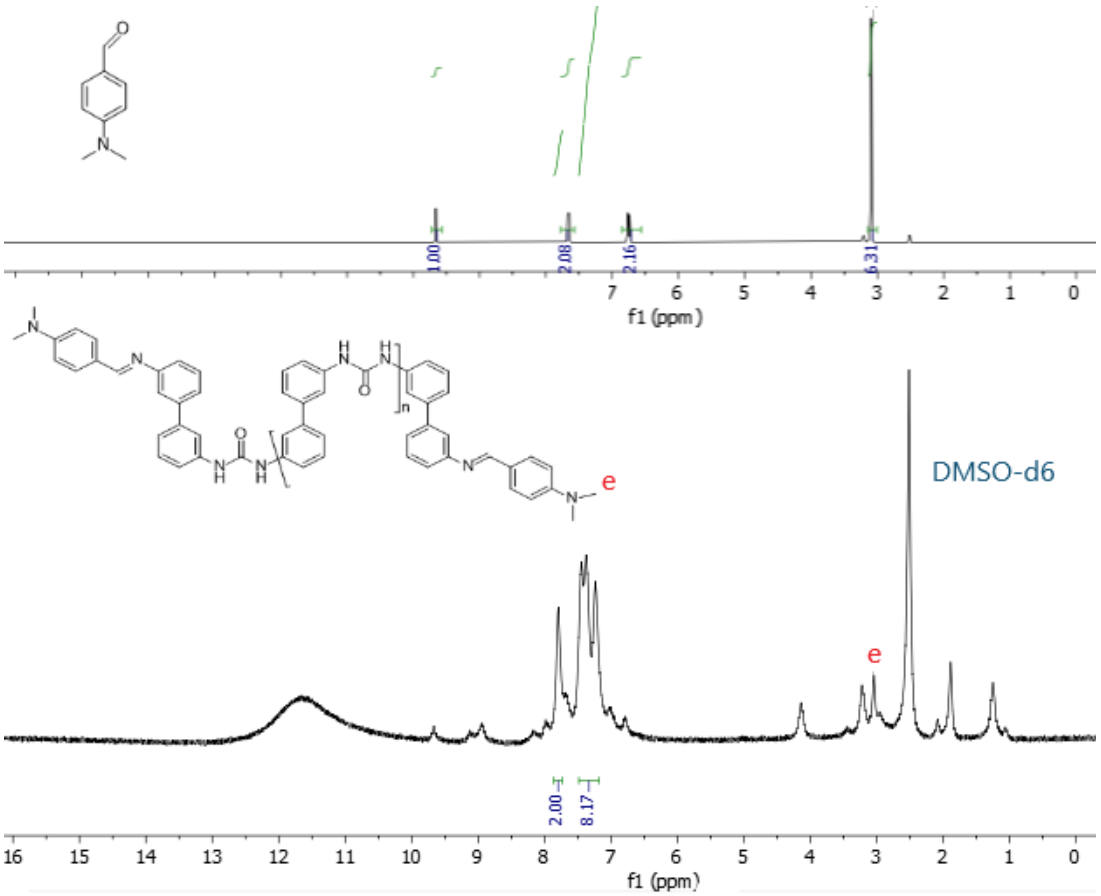


Figure S5. ^{1}H NMR spectrum of the (8) in DMSO-d6 at r.t with N, N-dimethylamine moiety for determination molecular weight (Mn) of PUs .

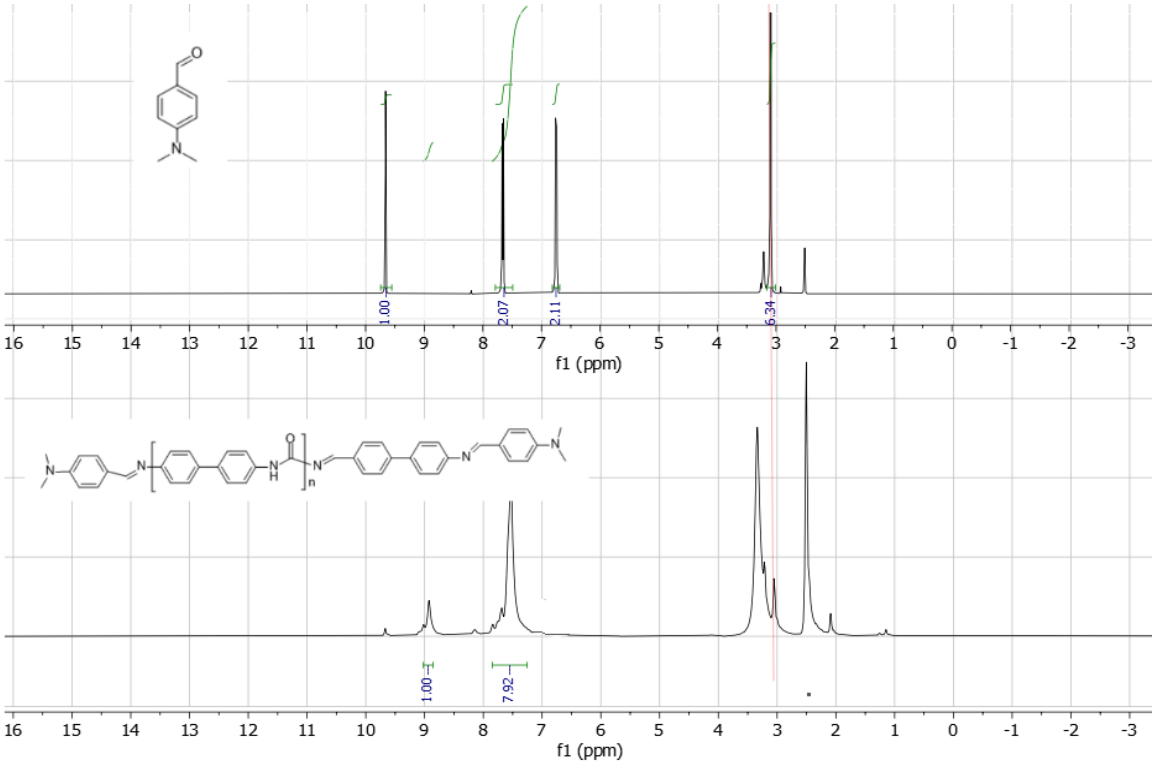


Figure S6. ^{1}H NMR spectrum of the (9) in DMSO-d_6 at r.t with N, N-dimethylamine moiety for determination molecular weight (Mn) of PUs.

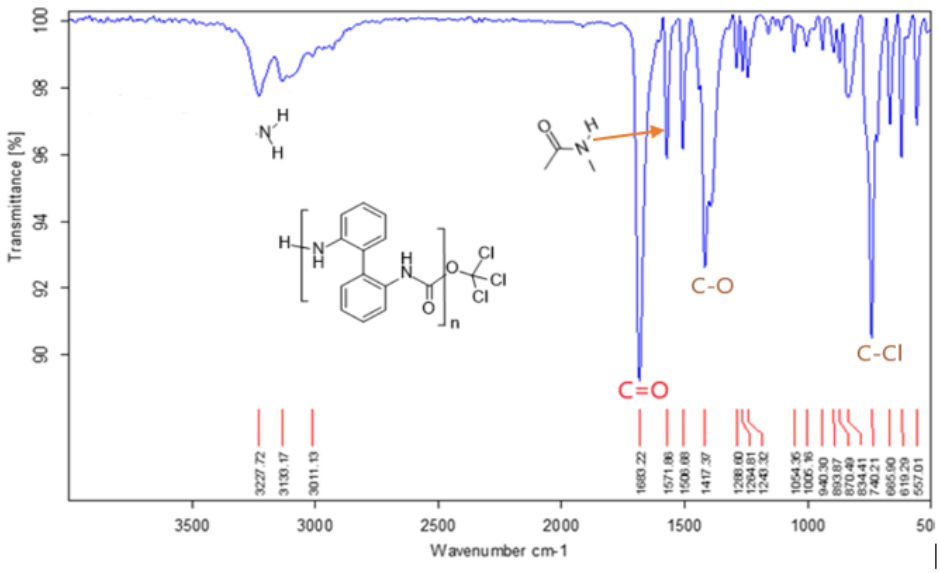


Figure S7 IR spectrum of PU (4)

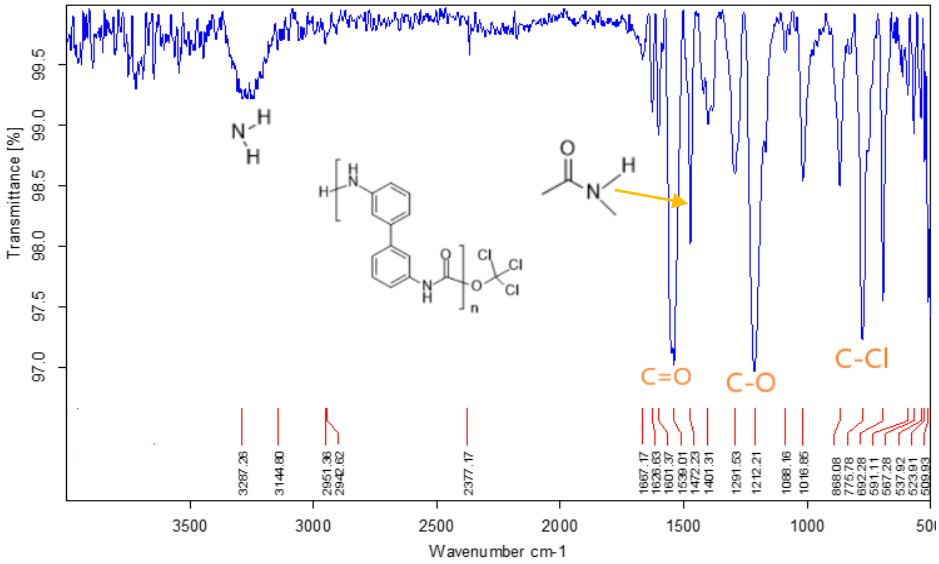


Figure S8 IR spectrum of PU (5)

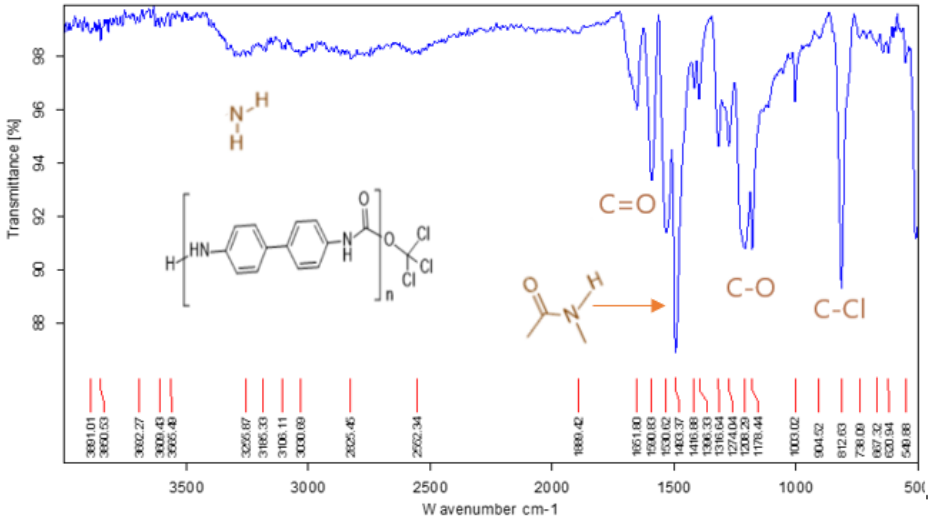


Figure S9 IR spectrum of PU (6)

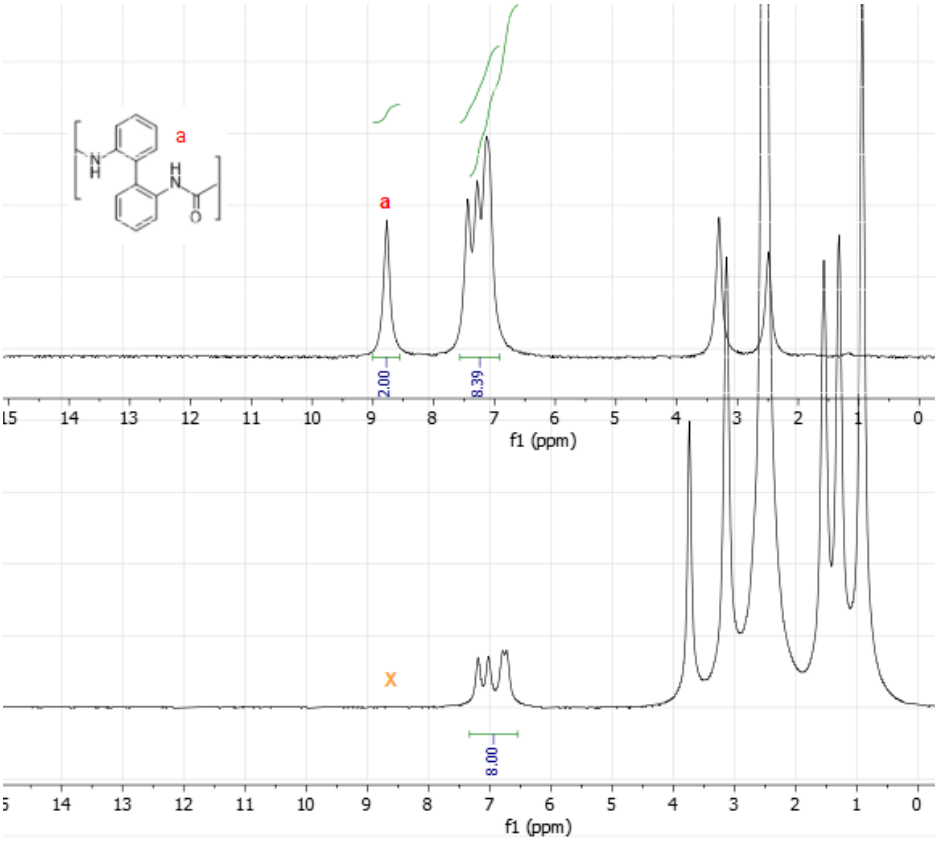


Figure S10. ^{1}**H NMR spectrum of the (4) in DMSO-d_6 at r.t. with additional TBAOH**

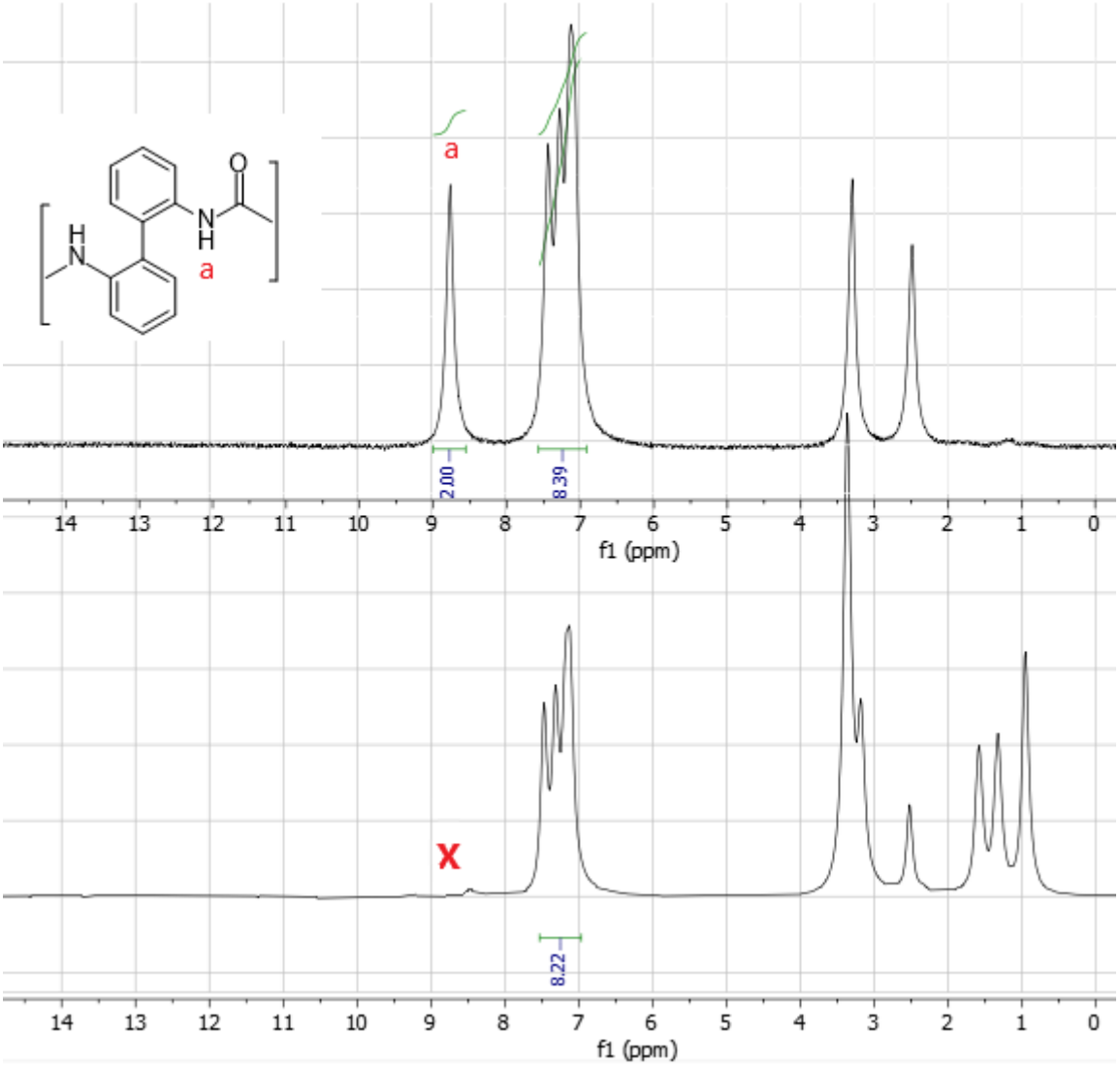


Figure S11. ^{1}**H NMR spectrum of the (4) in DMSO-d_6 at r.t. with additional TBAF**

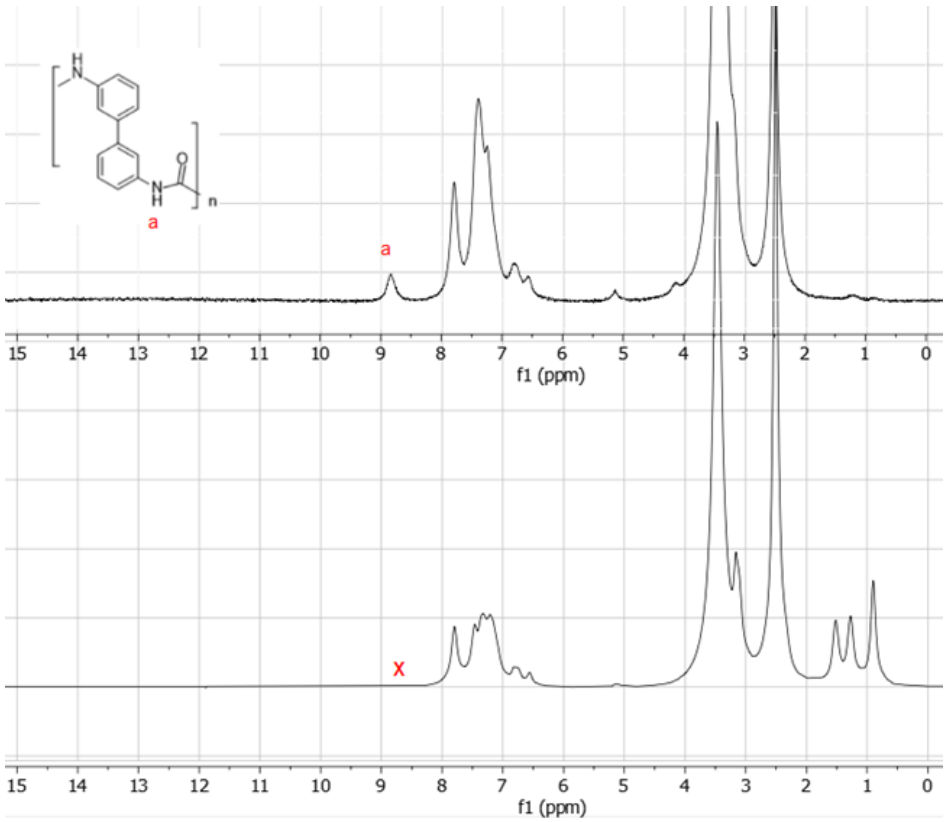


Figure S12. ^{1}H NMR spectrum of the (5) in DMSO-d_6 at r.t. with additional TBAOH

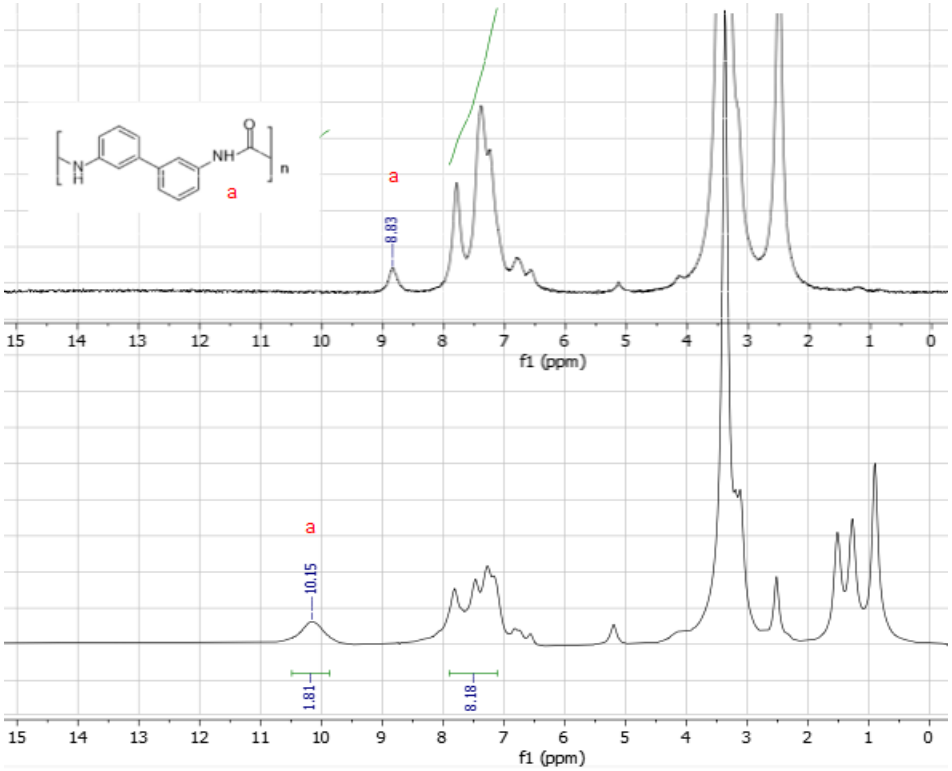


Figure S13. ^{1}H NMR spectrum of the (5) in DMSO-d_6 at r.t. with additional TBAF

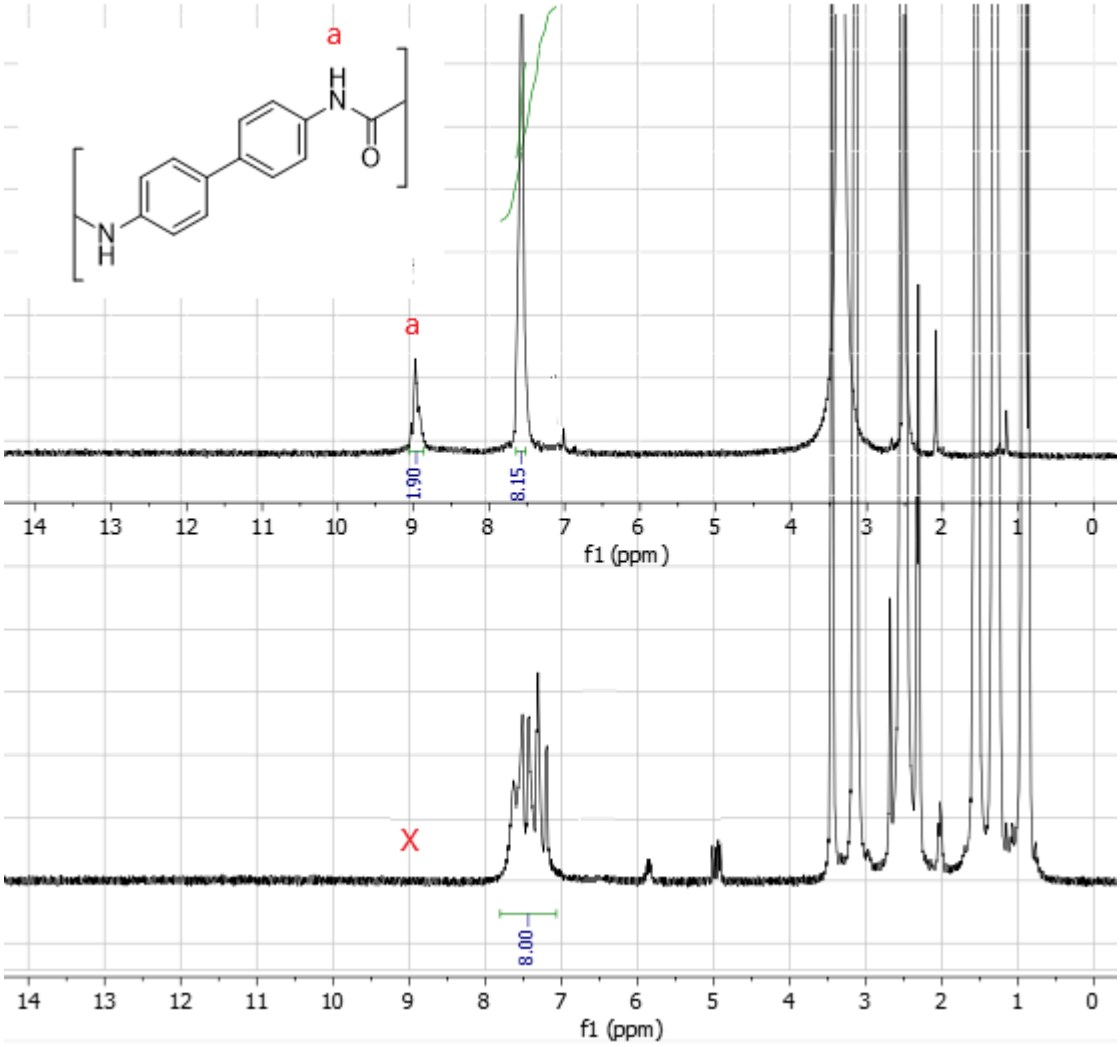
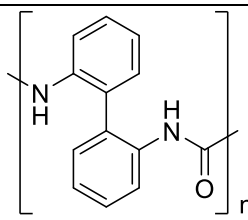
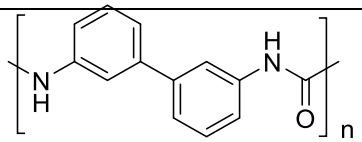
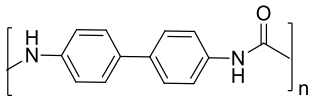


Figure S14. ^{1}**H NMR spectrum of the (9) in DMSO-d_6 at r.t. with additional TBAOH**

Table S1 Photophysical properties of the PUs 4, 5, 6 and their complexes with F (-)

Polymer/complex		**Absorption maxima, nm**	**Emission maxima, nm**
4		297	430
4+F(-)		340 (sh)	432, 551
5		299 (sh)	352, 406

5+F(-)		319	508
6		327 (pl)	365 (pl)
6+F(-)		340 (sh)	385

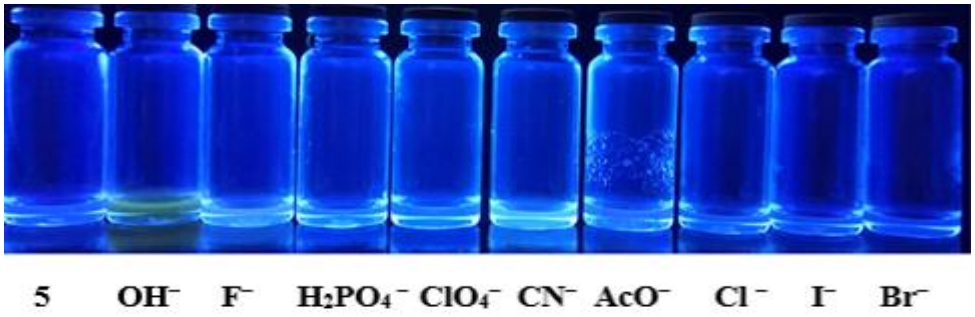


Figure S15. Fluorescence response of PU 4

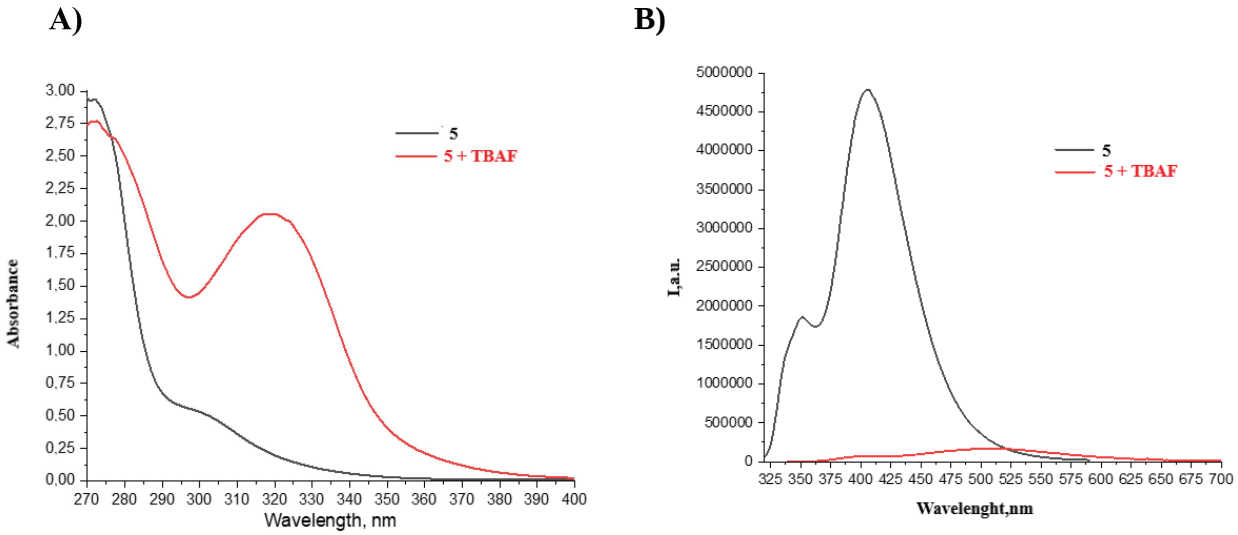


Figure S16. Change in absorption (A) and emission (B) spectra of PU 5 in DMSO in the presence of TBAF.

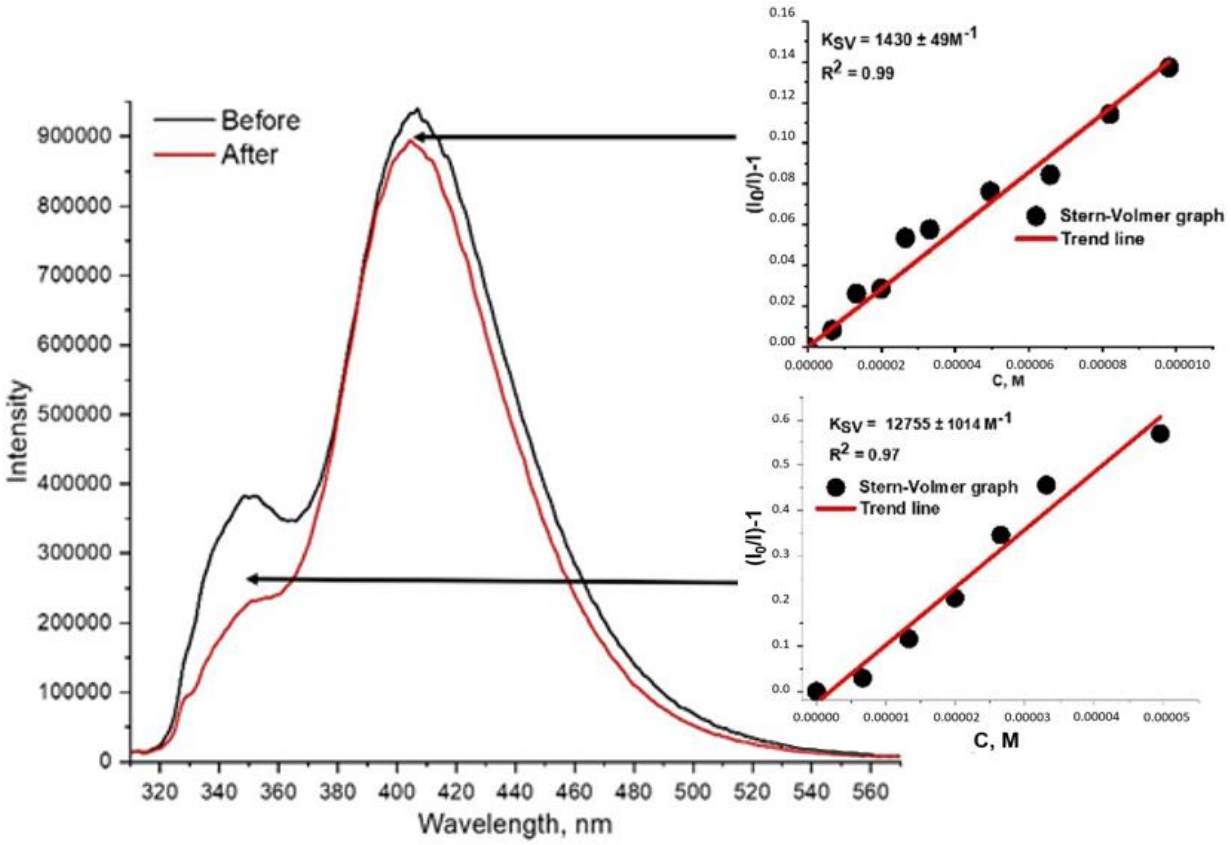


Figure S17. Fluorescence quenching effect of TBAF on the PU (5).

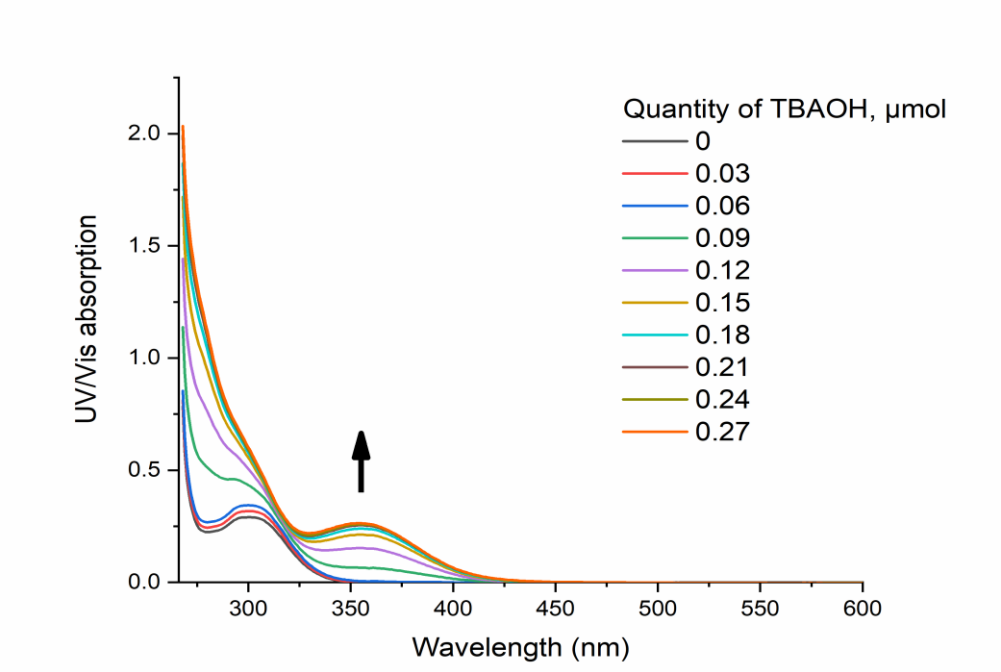


Figure S18. Change in absorption of PU (4) in DMSO in the presence of TBAOH.

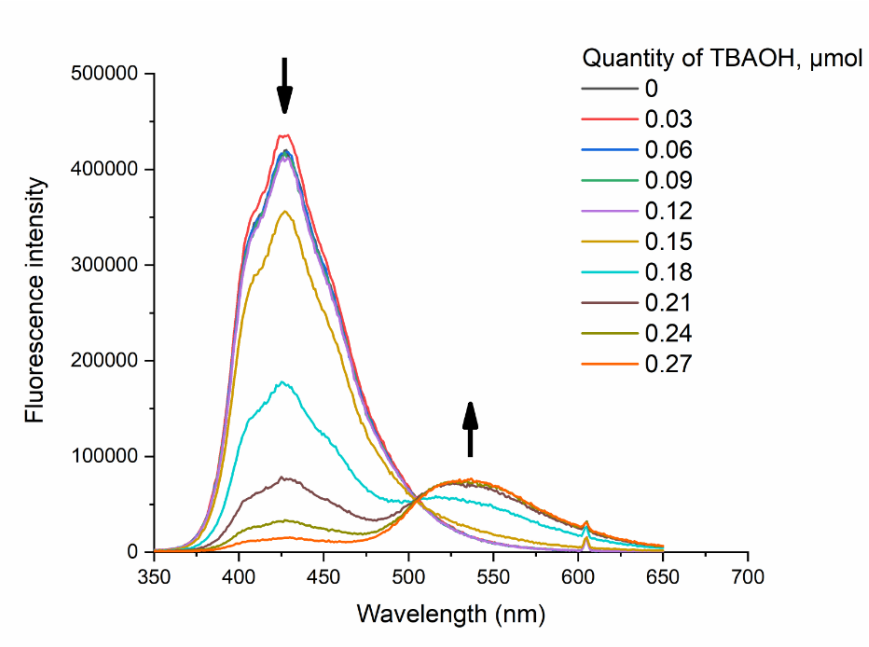


Figure S19. Change in emission PU (4) in DMSO in the presence of TBAOH.

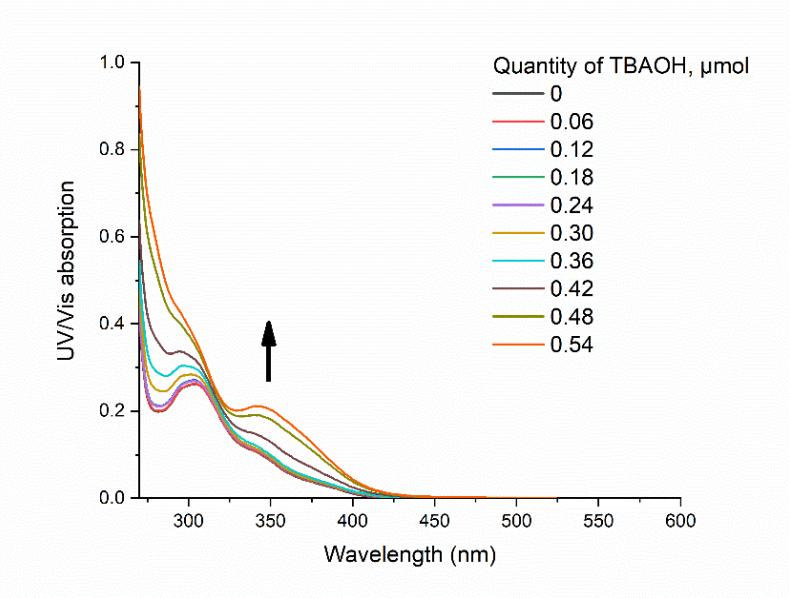


Figure S20. Change in absorption of PU (7) in DMSO in the presence of TBAOH.

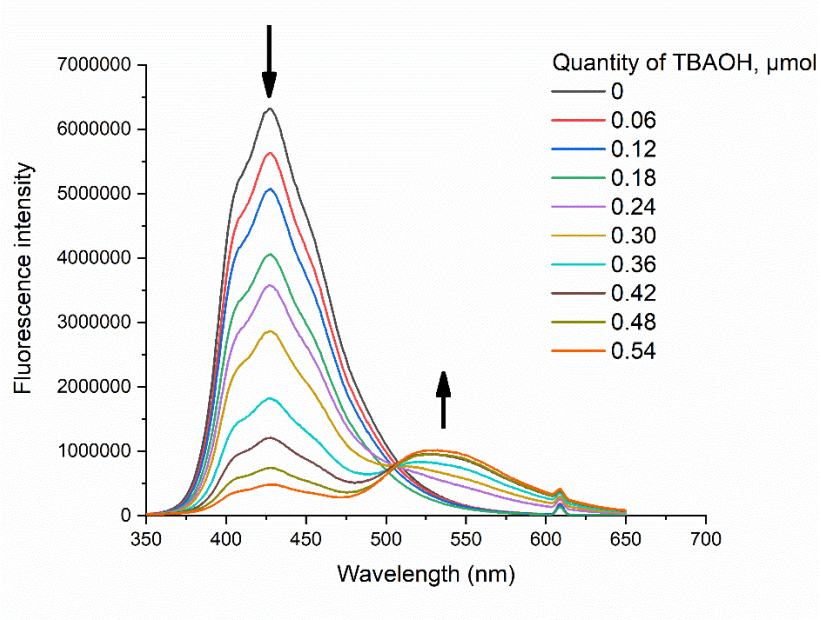
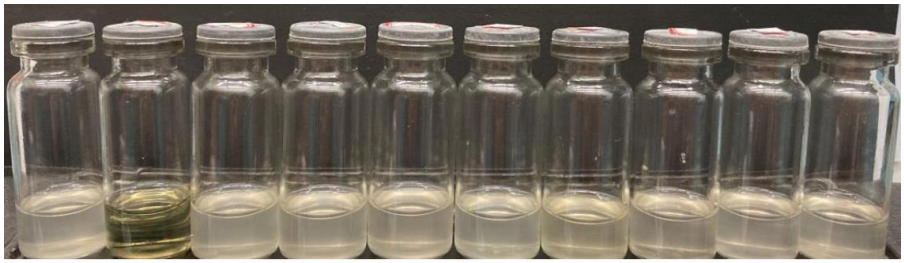


Figure S21. Change in emission PU (7) in DMSO in the presence of TBAOH.



Free OH^- F^- $H_2PO_4^-$ ClO_4^- CN^- AcO^- Cl^- I^- Br^-

Figure S22. Colorimetric response of PU 6 towards anions in DMSO solution under Daylight.



Free OH^- F^- $H_2PO_4^-$ ClO_4^- CN^- AcO^- Cl^- I^- Br^-

Figure S23. Fluorescence response of PU 6 toward anions in DMSO solution under UV (λex = 365 nm).



Figure S24. Colorimetric response of PU 8 towards anions in DMSO solution under Daylight

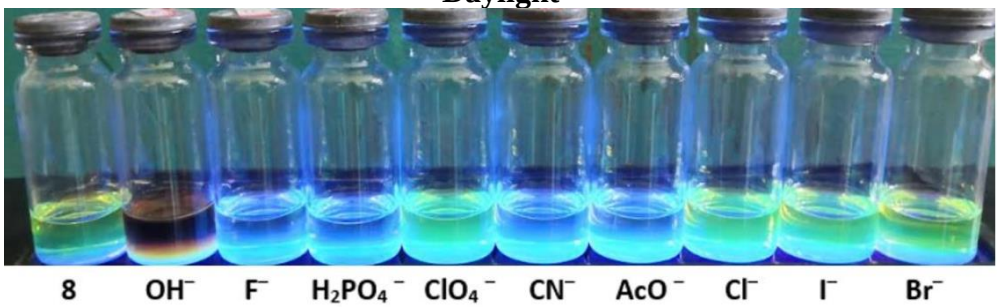


Figure S 25. Fluorescence response of PU 8 toward anions in DMSO solution under UV (λex = 365 nm).



Figure S26. Colorimetric response of PU 9 towards anions in DMSO solution under Daylight

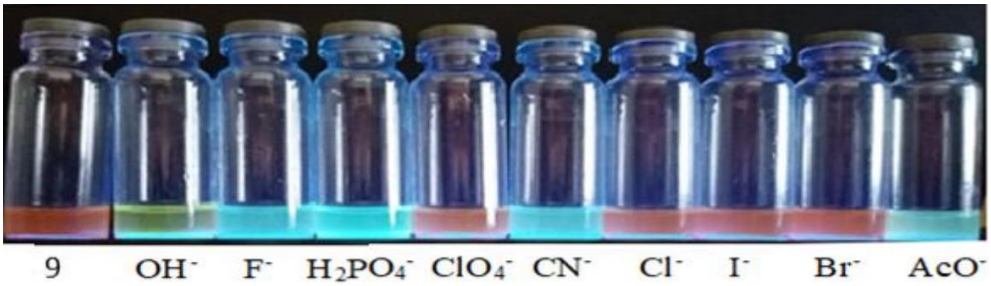


Figure S27. Fluorescence response of PU 9 toward anions in DMSO solution under UV (λex = 365 nm)

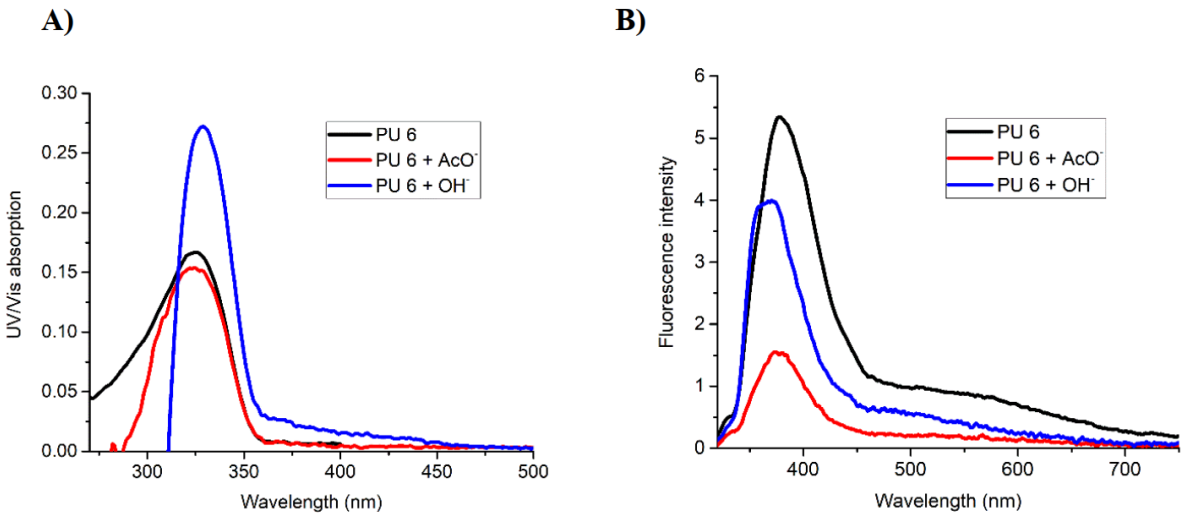


Figure S28. Change in absorption (A) and emission (B) spectra of PU 6 in DMSO in the presence of various anions.

General method for the synthesis of Polyurea's 7-9.

Isomeric 2,2(1)-, 3,3(2)- or 4,4 (3) -diaminobiphenyls (1 eq.), triphosgene (1.5 eq), 4-N,Ndimethylaminobenzaldehyde (0.1 eq) and K_2CO_3 (7 eq.) were reacted in 25 ml stainless still milling jar with 4 balls 10 mm stainless still milling balls for 4 hours at a speed rotation of 500 rpm. After that the reaction mixture was washed by 10% aqueous solution of HCl, water, EtOH and acetone.

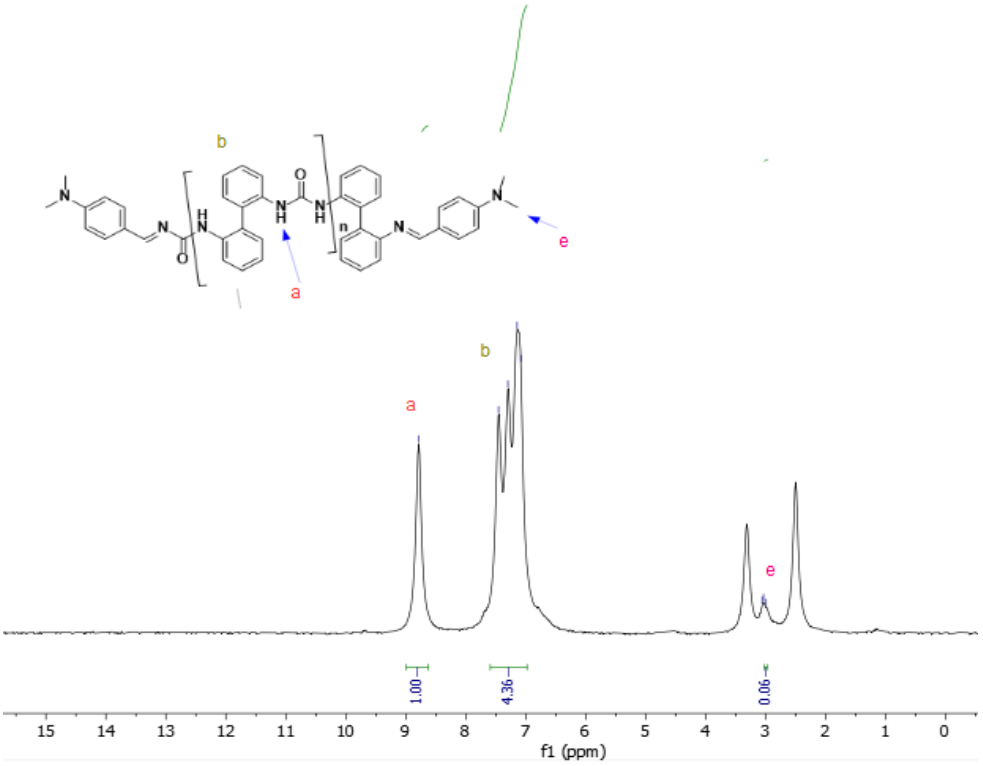


Figure S29. ^{1}H NMR of PU 7 in DMSO-*d*$_6$

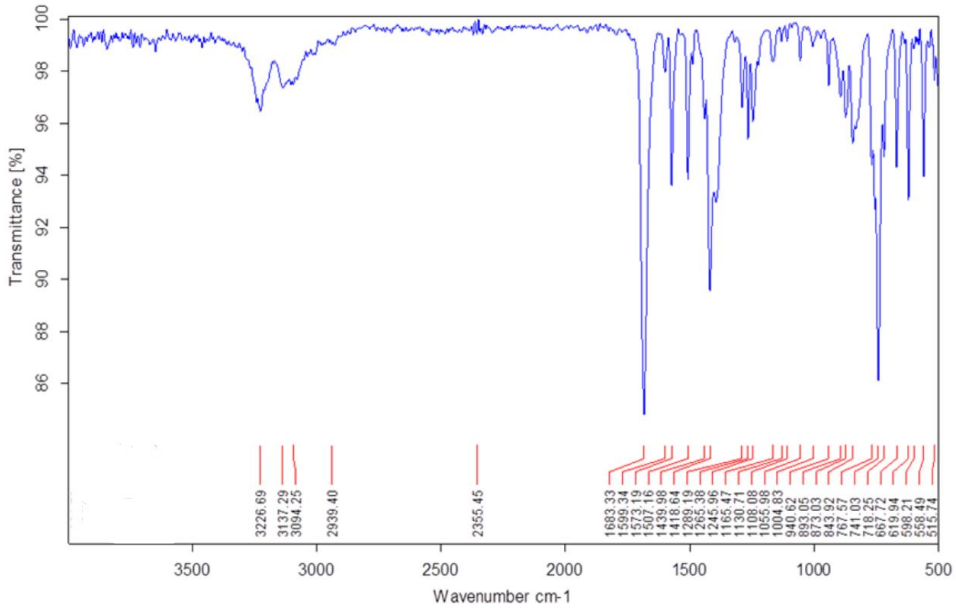


Figure S30. IR-spectra of PU 7

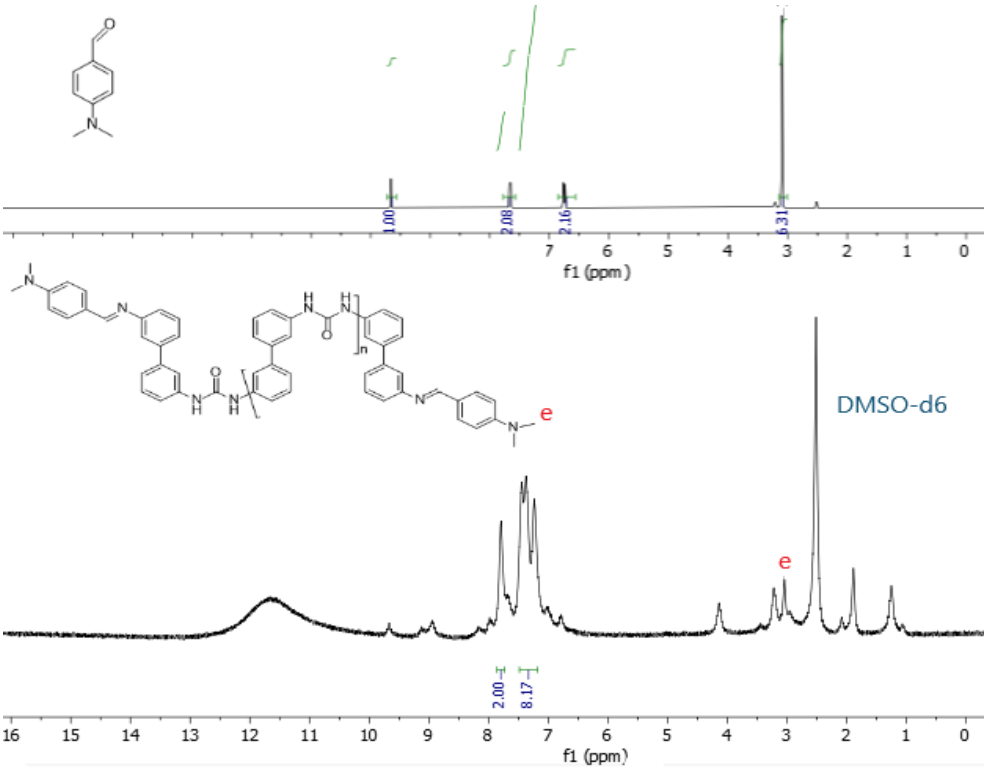


Figure S31. ^{1}H NMR spectra of PU 8 in DMSO-d_6

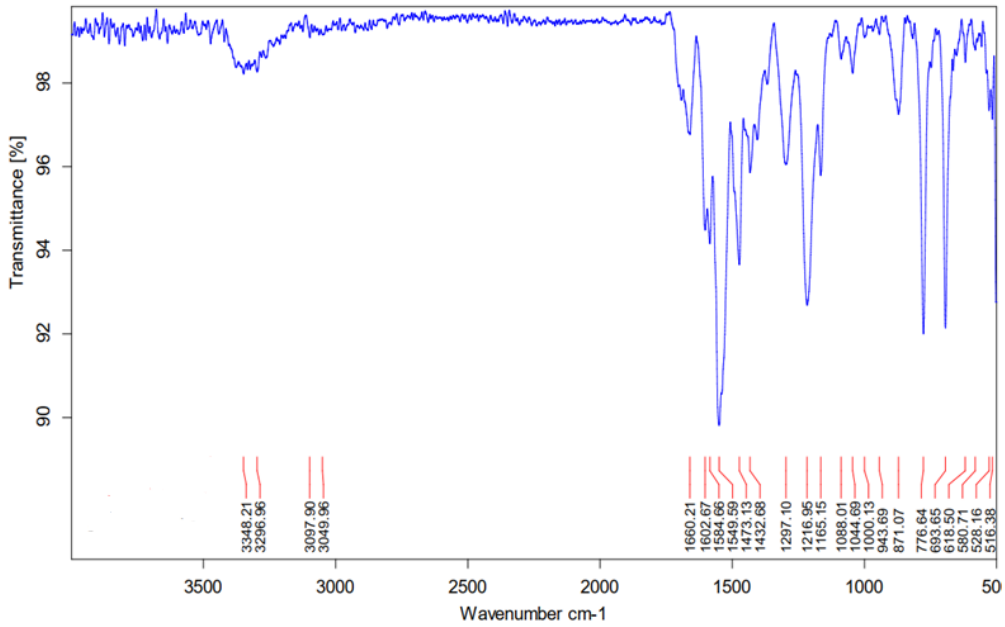


Figure S32. IR spectra of PU 8

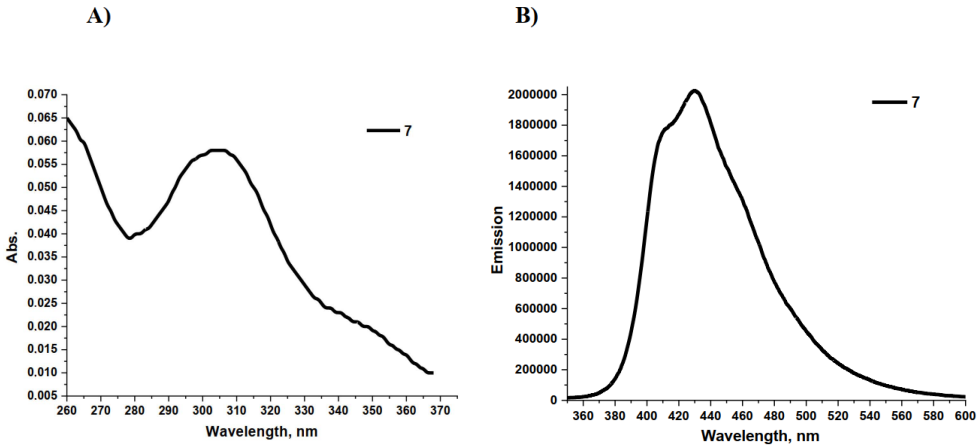


Figure S33:Absorption (A) and emission (B) spectra of PU 7 in DMSO

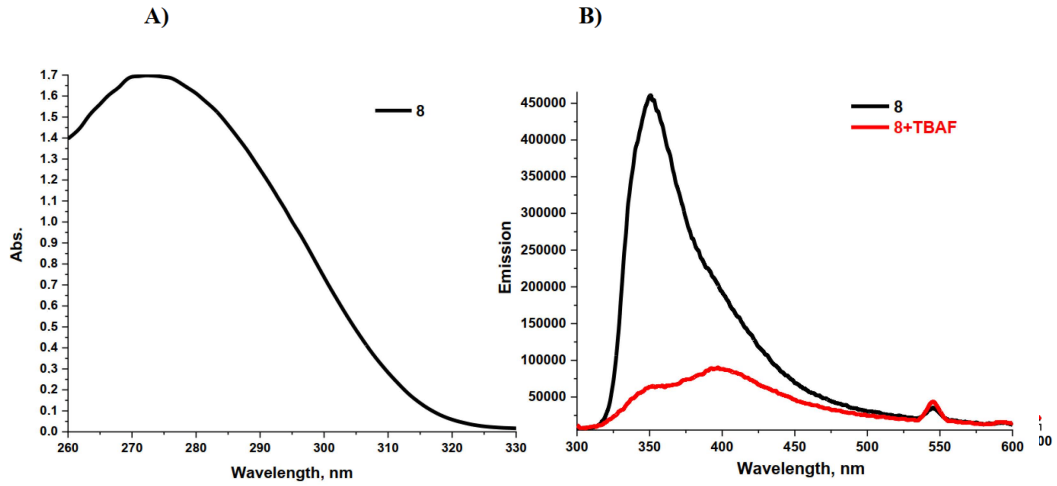


Figure S34. Absorption spectra (A) and change in emission spectra (B) of PU 8 in DMSO in the presence of TBAF

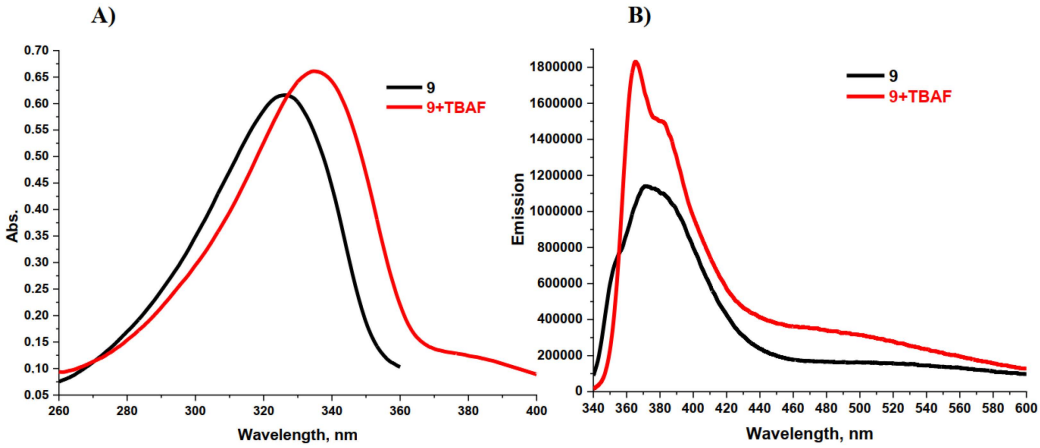
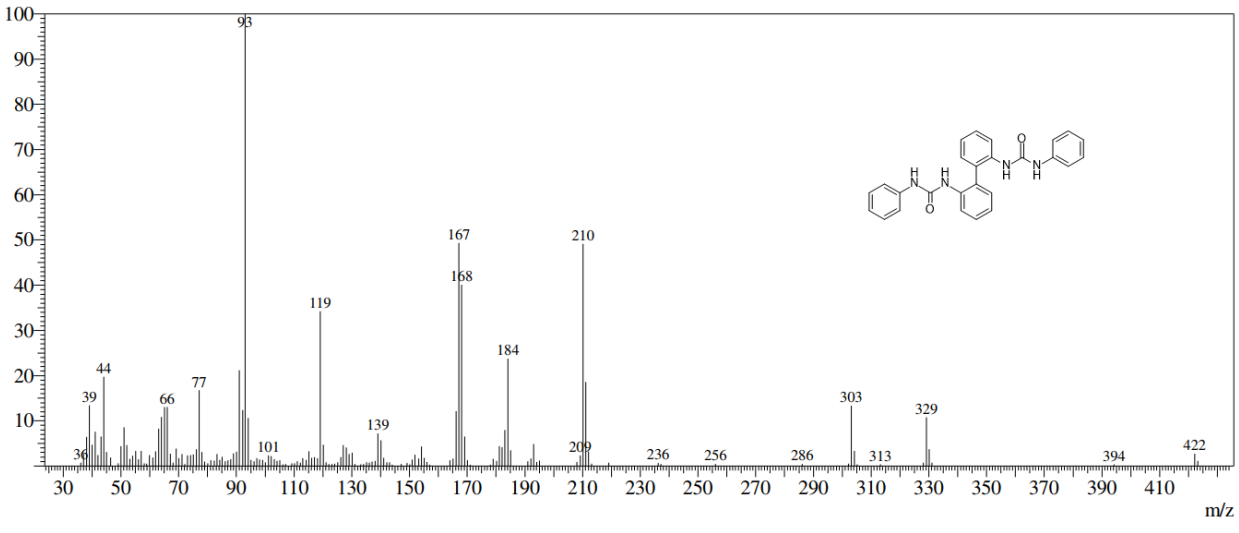


Figure S35. Change in absorption (A) and emission (B) spectra of PU 9 in DMSO in the presence of TBAF



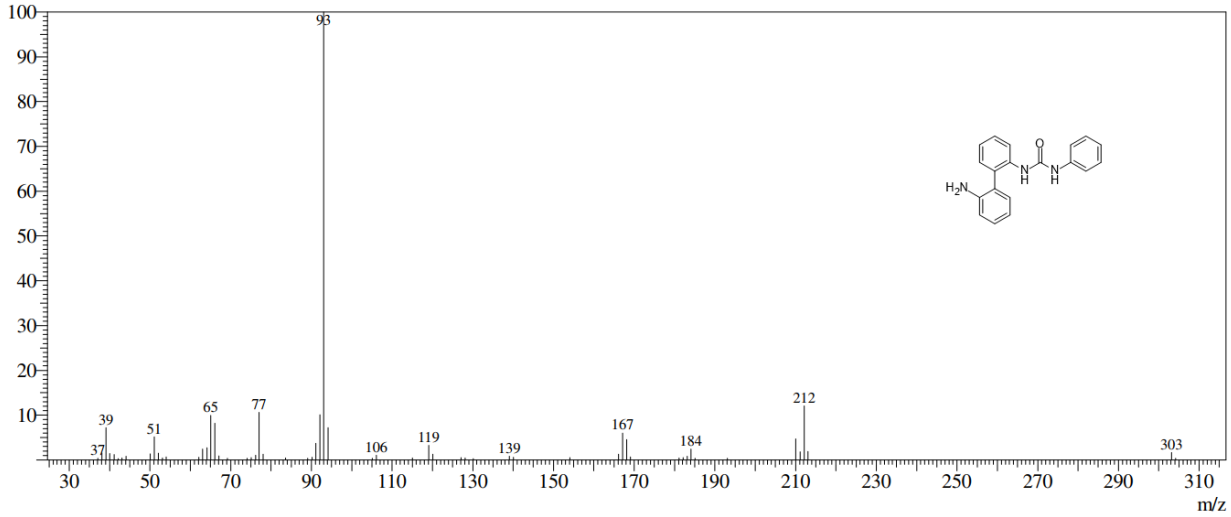


Figure S36. mass spectra of 1,1'-([1,1'-biphenyl]-2,2'-diyl)bis(3-phenylurea) and1-(2'-amino-[1,1'-biphenyl]-2-yl)-3-phenylurea.

Table S2. Results of intraday and interday experiments on synthesis of PUs

	PU4	PU5	PU6
Intraday			
Mean ± SD	75.67 ± 1.2472	68.67 ± 0.9428	93.00 ± 1.6330
RSD	2.02	1.68	2.15
Interday			
Mean ± SD	76.00 ± 0.8165	68.33 ± 1.6997	93.67 ± 1.2472
RSD	1.32	2.22	1.63
p-value			
p-value	0.42	0.29	0.85

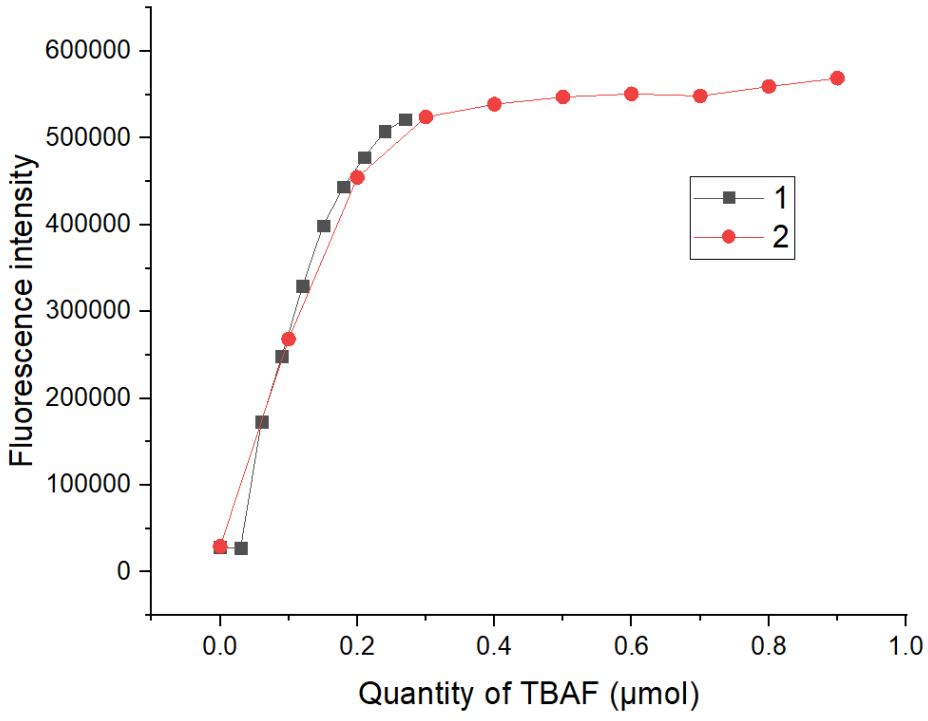


Figure S37. Change of FL emission intensity of PU **4** at 530 nm with different aliquot of TBAF Table S3. Data for Figure S37.

# 1		# 2	
Quantity of TBAF in µmol	FL Intensity	Quantity of TBAF in µmol	FL Intensity
0	28250	0	29456
0.03	27826	0.1	268320
0.06	172610	0.2	454730
0.09	248880	0.3	524140
0.12	329080	0.4	539040
0.15	399070	0.5	547310
0.18	444050	0.6	551000
0.21	477810	0.7	548640
0.24	507790	0.8	559430
0.27	521710	0.9	568290

Computational details

The quantum chemical calculations including full geometry optimization of all model structures were carried out at the ωB97XD/CEP-121G level of theory with the help of the Gaussian-09 program package [1]. No symmetry restrictions were applied during the geometry optimization procedure. The Hessian matrices were calculated analytically for all optimized model structures to prove the location of correct minima on the potential energy surface (no imaginary frequencies were found in all cases).

Table S4. Calculated Gibbs free energies for optimized equilibrium model structures

Model structure	Gibbs free energy, a.u.
ACO^-	-45.022612
Br^-	-13.481468
Cl^-	-15.004344
ClO_4^-	-78.305417
CN^-	-15.528862

F^-	-24.170916
$H_2PO_4^-$	-71.560313
I^-	-11.559448
OH^-	-16.504252
PU4···ACO^-	-161.269585
PU4···Br^-	-129.712888
PU4···Cl^-	-131.244522
PU4···ClO_4^-	-194.521853
PU4···CN^-	-131.770029
PU4···F^-	-140.461544
PU4···$H_2PO_4^-$	-187.795341
PU4···I^-	-127.783640
PU4	-116.200781
PU4···OH^-	-132.801763
PU5···ACO^-	-161.278974
PU5···Br^-	-129.720983
PU5···Cl^-	-131.252858
PU5···ClO_4^-	-194.526387
PU5···CN^-	-131.778292
PU5···F^-	-140.467525
PU5···$H_2PO_4^-$	-187.799701
PU5···I^-	-127.792294
PU5	-116.199835
PU5···OH^-	-132.810579
PU6···ACO^-	-161.280317
PU6···Br^-	-129.721682
PU6···Cl^-	-131.253835
PU6···ClO_4^-	-194.528556
PU6···CN^-	-131.780227
PU6···F^-	-140.468666
PU6···$H_2PO_4^-$	-187.804323
PU6···I^-	-127.792007
PU6	-116.200136
PU6···OH^-	-132.811808

References.

1. 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.; et al. Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.