SUPPORTING INFORMATION

Waterborne Polyurethanes with Tunable Fluorescence and Room-Temperature Phosphorescence

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Part I. Materials, methods, and syntheses

Materials. Isophorone diisocyanate (IPDI) was purchased from Junsei Chemical Co., Ltd. Polytetramethylene ether glycol (PTMG, M_n = 2000) was supplied by Dacicel Chemical Industries, Ltd. and thoroughly dehydrated at 110 °C before use. 1,4-Butanediol (BDO) and 2,2-dimethylolpropionic acid (DMPA) were purchased form Sigma-Aldrich Co.,Ltd. Dibutyltin dilaurate (DBTDL), triethylamine (TEA), acetone, diethanolamine and potassium hydroxide were purchased from Shanghai Chemical Reagent Co., Ltd. 4-Chlorobenzophenone was supplied by Energy Chemical Co., Ltd.

Methods. ^{1}H and ^{13}C NMR spectra were obtained on Bruker Avance 300 MHz NMR spectrometers using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. UV/vis absorption spectra were measured using a UV-3600 spectrophotometer in tetrahydrofuran (THF) and water at 298 K. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor27 FTIR spectrometer in the range of 4000-500 cm^{-1} using thin film prepared by casting emulsion of NBP-WPU on KBr a flake and then evaporating water by heating under an infrared lamp. The spectra of photoluminescence excitation and emission were determined at room temperature on a Horiba Fluorolog-3 spectrofluorometer. The lifetimes of fluorescence and phosphorescence were acquired with a NanoLED and a SpectraLED laser with the excitation peak at 369 nm, respectively. Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). The quantum yields of solutions were measured at room temperature using quinine sulfate (Φ = 0.54) as a reference.[1] The quantum yields of solid powders and films were measured on a Fluorolog-3-TAUfluorescence spectrophotometer equipped with a $BaSO_4$-coated integrating sphere. Differential scanning calorimetric (DSC) curve was recorded using a Mettler-Toledo DSC1 at a constant heating rate of 10 °C/min from -50-150 °C. The thermogravimetric characteristics were investigated by a thermogravimetric analyzer (TGA) of Shimadzu TGA-50 under a nitrogen atmosphere. Gel permeation chromatography (GPC) analyses were performed on a HP1100 (Ultraviolet–visible

detector) GPC instrument and calibrated with ploystyrene, at a constant column temperature of 40 °C. The eluent was THF, and flow rate was 1.0 mL/min. The average particle size of the emulsions was determined by using a Zetasizer Nano-ZS-90 instrument.

Preparation of K1 and Waterborne polyurethane SDMs

{4-[Bis(2- hydroxyethyl)amino]phenyl}(phenyl)methanone (**K1**)

A 100-mL three-neck flask was charged with 4-chlorobenzophenone (4.32 g, 20 mmol) and diethanolamine (14.32 g, 136 mmol) and potassium hydroxide (1.46 g, 26 mmol). The flask was heated at 130 °C for ~14 h. After cooling to room temperature, the dark viscous reaction mixture was poured into water (100 mL). The resulting suspension was thoroughly extracted with dichloromethane (50 mL×3). The aqueous phase was discarded and the crude organic extract was concentrated and purified by passing through a silica gel column (eluent: ethyl acetate). The eluted yellow solution was evaporated and the oily residue was dried *in vacuo* to afford {4-[bis(2-hydroxyethyl)amino]phenyl} (phenyl) methanone (yellow-brown solid, 2.23 g, 40 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.88 H_Z, 2H), 7.71 (m, 2H), 7.56 (m, 1H), 7.46 (t, J = 7.37 H_Z, 2H), 6.83 (d, J = 8.22 H_Z, 2H), 3.92(t, J = 4.8 H_Z, 4H), 3.71 (t, J = 4.8 H_Z, 4H). ^{13}C-NMR (75 MH_Z, $CDCl_3$): δ 195.53, 151.55, 138.79, 132.87, 131.46 (2C), 129.46 (2C), 128.09 (2C), 124.98, 111.12 (2C), 60.25 (2C), 55.03 (2C).

Waterborne polyurethanes **SDM1 – SDM20**

The preparation process of **SDMs** is shown in Scheme 1. A 100 mL round-bottom, three-necked flask with a mechanical stirrer, thermometer, condenser was used as the reactor. The reactants IPDI and PTMG (M_n = 2000) were added into the reactor and the molar ratio was specified in Table 1 for different samples. The flask was heated to 90 °C and the NCO content was determined using a standard dibutylamine titration method.[2] DMPA was then added into the mixture and reacted at 80 °C. Subsequently,

BDO and **K1** were put into the flask and reacted at 70 ℃ for 1 h. Afterward a trace amount of catalyst DBDTL (0.05–0.1 wt%) was needed and kept at 70 °C for 4 h. During the prepolymerization, a moderate amount of acetone was required to reduce the viscosity. As a neutralization agent, the acetone solution of TEA (8 wt%) was then added into the mixture and reacted with the carboxylic group on the side chain of the polyurethane prepolymer for 10 min to form a quaternized NCO-terminated prepolymer. Finally, the highest shearing speed of stirrer (2500 r/min) was used to emulsify the solution for 30 min after suitable water was poured into the mixture. A off-white aqueous dispersion was obtained after acetone was removed *in vacuo*. The solid content of the obtained fluorescent dispersion was about 25 wt%. ^{1}H-NMR (400 MHz, $CDCl_3$) : 7.77- 6.83 (Ar-H), 3.8-4.1 (-COO-CH_2-), 3.3-3.5 (-OCH_2-,-N-CH_2-), 2.8-3.1 (-CH-,-CH_2-), 1.28-1.61 (-CH_2-), 0.93-1.05 (-CH_3).

Part II. Supplementary Figures.

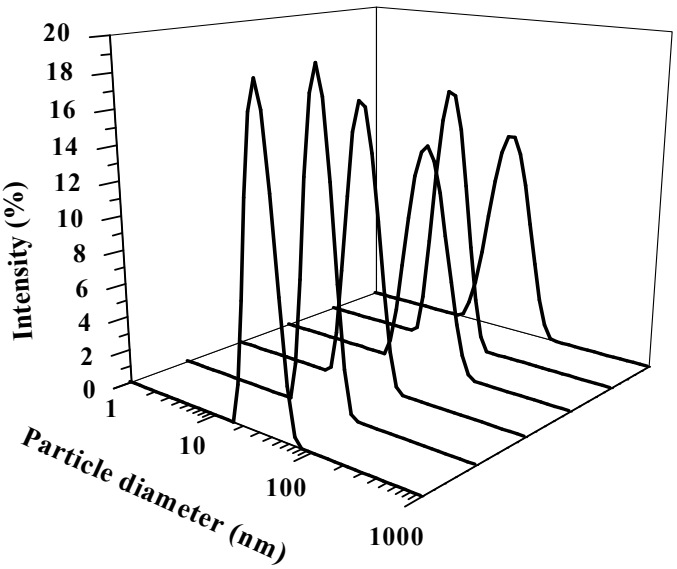


Figure S1. Particle-size distribution for the aqueous dispersions of **SDM0** (31.73 nm), **SDM1** (31.56 nm), **SDM2** (24.65 nm), **SDM5** (35.16 nm), **SDM 10** (21.83 nm), and **SDM20** (31.92 nm)

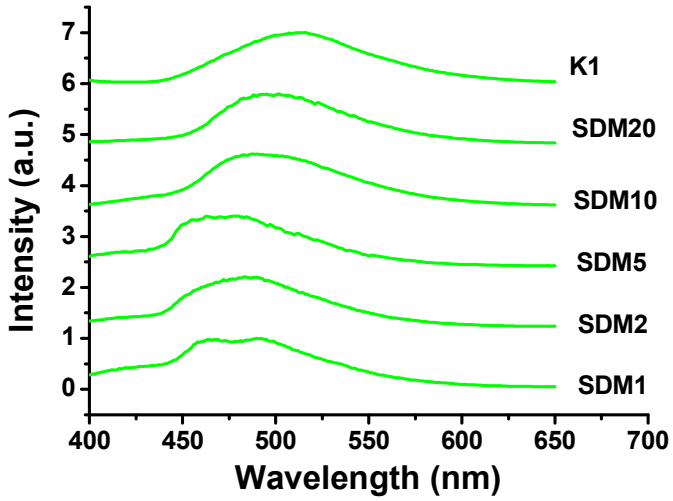


Figure S2. Evolution of steady-state emission spectra of **SDM1-SDM20** films and **K1** at 77 K.

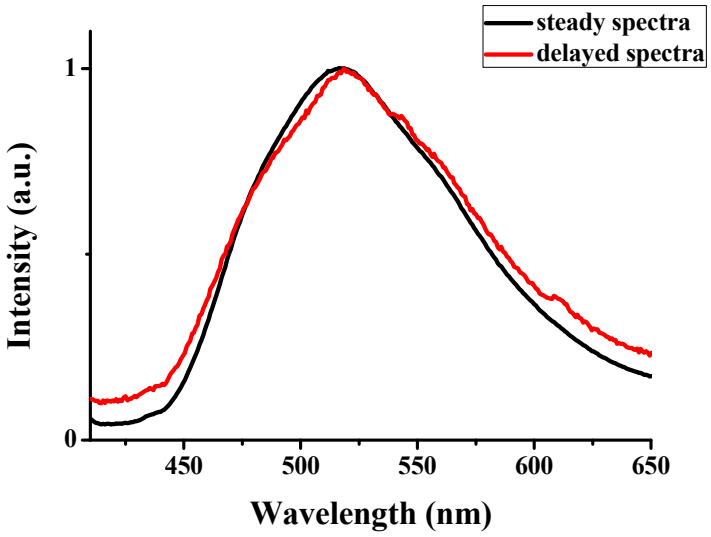


Figure S3. Steady-state and delayed emission spectra of K1 at 77K.

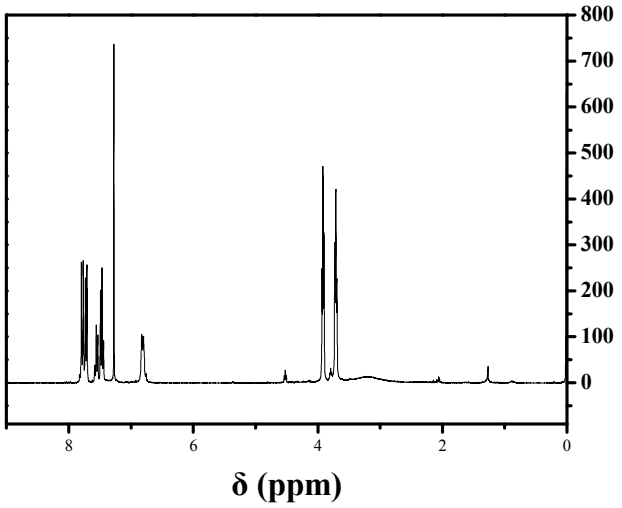


Figure S4. ^{1}H NMR spectrum of **K1** in $CDCl_3$.

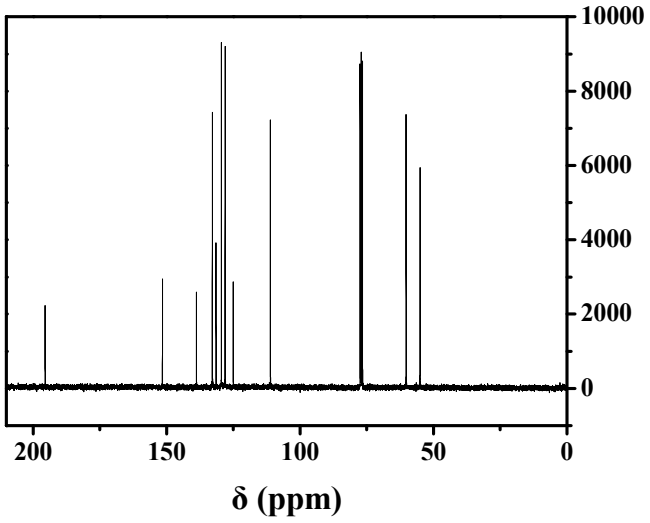


Figure S5. ^{13}C NMR spectrum of **K1** in $CDCl_3$.

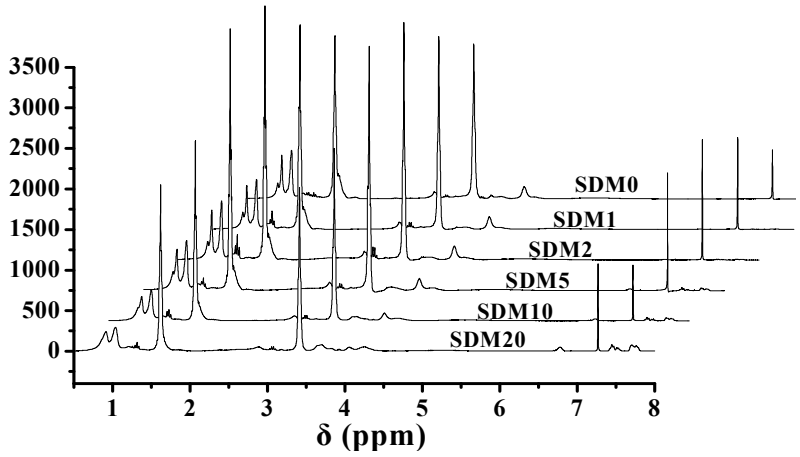


Figure S6. ^{1}H NMR spectra of **SDM0-SDM20** in $CDCl_3$.

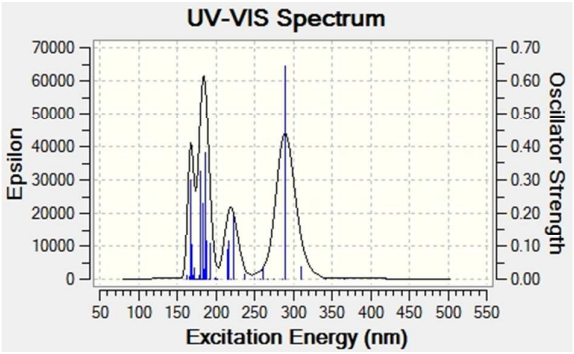


Figure S7. The computed absorption spectrum of K1

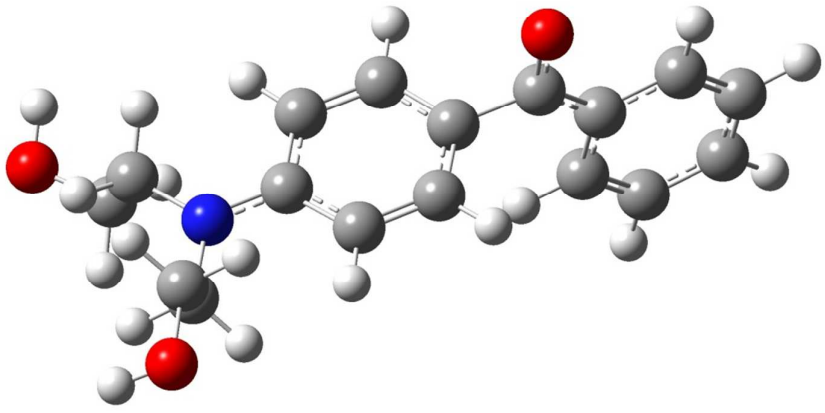


Figure S8. Excited singlet structure of **K1**.

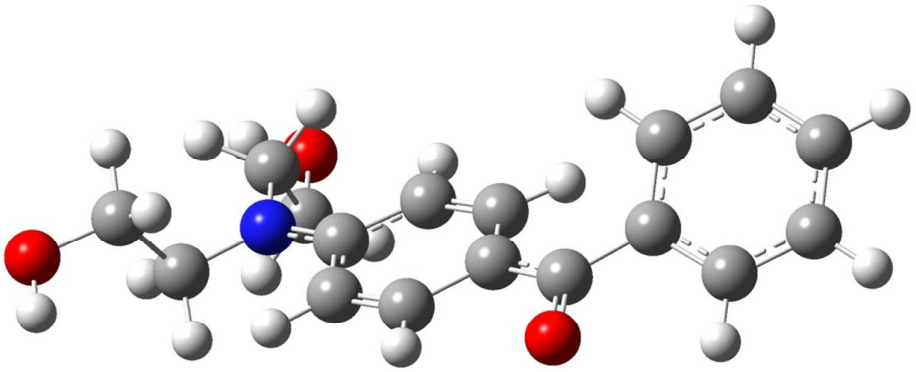


Figure S9. Triplet structure of **K1**.

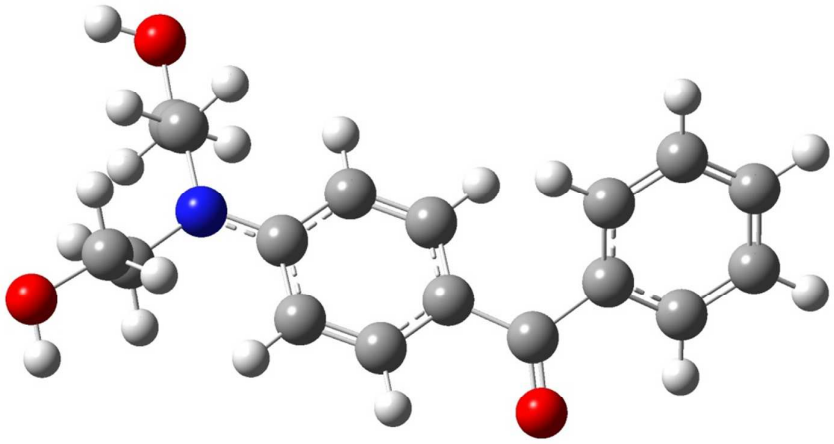
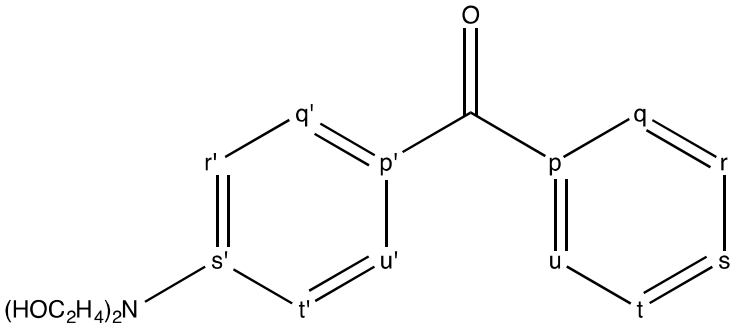
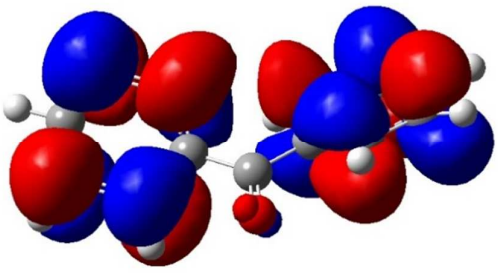


Figure S10. Ground state (singlet) of **K1**.

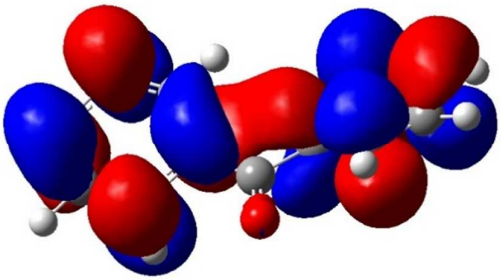
Table S1. Geometric parameters (Angstroms, ^{o}) of **K1**.



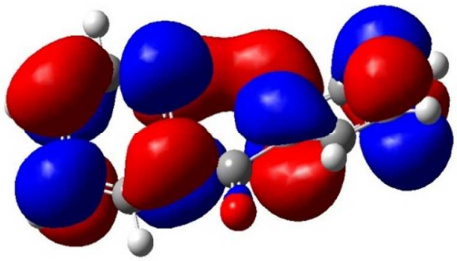
Parameter	S_0	S_1	T_1
CO	1.221	1.360	1.273
C-p	1.495	1.417	1.489
p – q	1.387	1.419	1.404
q - r	1.384	1.385	1.393
r - s	1.384	1.399	1.393
s - t	1.386	1.399	1.395
t – u	1.380	1.385	1.389
u - p	1.388	1.420	1.404
C - p'	1.481	1.479	1.489
p'– q'	1.413	1.419	1.404
q' – r'	1.374	1.385	1.393
r'– s'	1.425	1.399	1.393
s'- t'	1.386	1.399	1.395
t' – u'	1.373	1.385	1.389
u – p'	1.389	1.449	1.404
N-s'	1.380	1.360	1.373



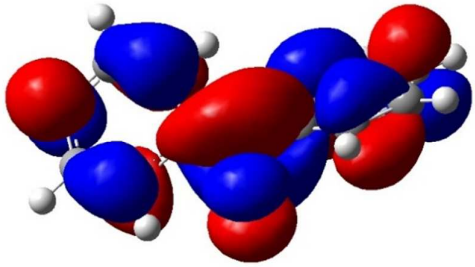
#52: C2- antisymmetric (b) combination of benzene pi* (antibonding) MOs; descended from b1 in C2v. E = +0.03745



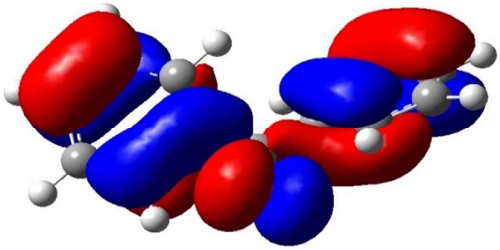
#51: C2- symmetric (a) combination of benzene pi* antibonding MOs; descended from a2 in C2v. E = +0.03129



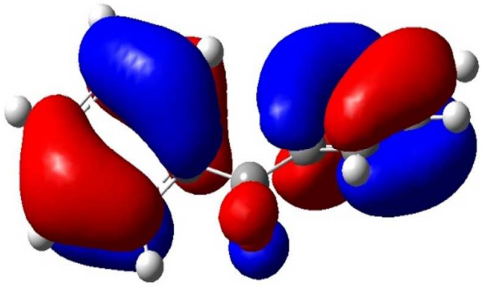
#50: a(2) Benzene pi*. E = 0.02475



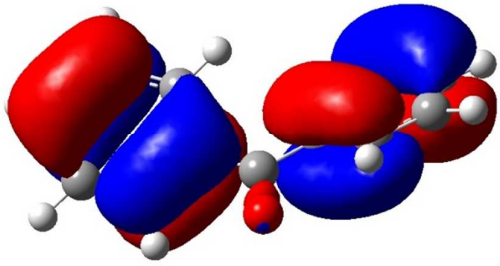
#49: b(1) pi* on CO with stabilizing admixture of benzene Lowest Unoccupied MO. E = -0.02409



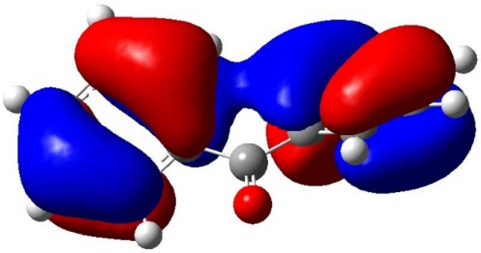
#48: b(2) O lone pair (pseudo-pi) with destabilizing admixture from benzene pi bonding MOs = “n”. E= -0.31045.



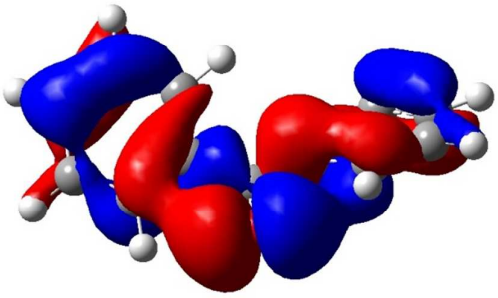
#47: b(1) combination of benzene pi (bonding) MOs. E= -0.31711



#46: a (2) combination of benzene pi bonding MOs. E = -0.31799

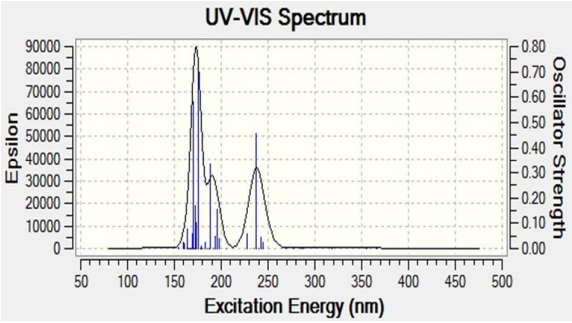


#45: a(2) combination of benzene pi bonding MOs. E = -0.32100



#44: -0.32985 H b(2) mainly lone pair with some benzene admixture made possible by descent in symmetry

(next MO is much lower, -0.40943)



Triplet 48 to 49 at 401 nm (3.09 eV) nπ*
Triplet 46 to 49 at 366 nm (3.39 eV) ππ*
Triplet 44 to 49 at 355 nm (3.89 eV) nπ*
Singlet 44 to 49 at 318 nm (3.89 eV) nπ*
Triplet 47 to 49 at 288 nm (4.31 eV) ππ*
Triplet 45 to 49 at 285 nm (4.35 eV) ππ*-benz
Triplet mixed at 278 nm (4.47 eV)
Triplet 45 to 52, 46 to 49, 47 to 51 at 269 (4.61 eV)
Singlet 47 to 49 at 245 nm (5.06 eV) weak = 0.0258
Singlet 45 to 49 at 243 nm (5.15 eV) med = 0.0438
Triplet 46 to 42 at 238 nm (5.22 eV)
Singlet 46 to 49 at 235 nm (5.28 eV) str = 0.4550

Figure S11. MOs and Absorption spectrum for benzophenone.

Excited State 1: Triplet-A 3.0947 eV 400.63 nm f=0.0000
<S**2>=2.000

44 -> 53	0.11818
45 -> 50	-0.16972
46 -> 50	0.11815
46 -> 51	-0.20956
47 -> 49	0.15449
47 -> 52	-0.16075
48 -> 49	0.57359

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -576.236253374
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 3.3899 eV 365.75 nm f=0.0000
<S**2>=2.000

44 -> 51	0.14354
45 -> 49	-0.13438
45 -> 52	0.25361
46 -> 49	0.44783
46 -> 53	-0.10968
47 -> 50	0.28309
48 -> 50	0.11308
48 -> 51	-0.27150

Excited State 3: Triplet-A 3.4908 eV 355.17 nm f=0.0000
<S**2>=2.000

44 -> 49	0.57080
44 -> 53	0.11436
45 -> 50	0.18381
46 -> 51	0.17998
47 -> 49	-0.12722
47 -> 52	0.16218
48 -> 53	0.13864

Excited State 4: Singlet-A 3.8925 eV 318.52 nm f=0.0010
<S**2>=0.000

44 -> 49	0.50161
44 -> 53	0.14878
48 -> 49	0.45254
48 -> 53	0.11761

Excited State 5: Triplet-A 4.3100 eV 287.67 nm f=0.0000
<S**2>=2.000

44 -> 49	0.12791
45 -> 50	-0.21693
45 -> 51	0.22926
46 -> 51	0.15606
47 -> 49	0.56359
48 -> 49	-0.15248

Excited State 6: Triplet-A 4.3489 eV 285.09 nm f=0.0000
<S**2>=2.000

45 -> 49	0.54360
46 -> 49	0.20836

47 -> 50 -0.28500
47 -> 51 0.19130
48 -> 51 -0.13748

Excited State 7: Triplet-A 4.4583 eV 278.10 nm f=0.0000 <S**2>=2.000
40 -> 49 0.10186
44 -> 49 -0.24852
45 -> 50 0.31247
45 -> 51 0.23535
46 -> 50 0.13221
47 -> 52 0.35522
48 -> 49 0.23861
48 -> 52 -0.15864

Excited State 8: Triplet-A 4.6114 eV 268.86 nm f=0.0000 <S**2>=2.000
44 -> 50 0.10708
45 -> 49 0.16531
45 -> 52 0.34616
46 -> 49 -0.32484
46 -> 52 0.16726
47 -> 50 0.22625
47 -> 51 0.31217
48 -> 50 -0.23591

Excited State 9: Singlet-A 5.0569 eV 245.18 nm f=0.0258 <S**2>=0.000
44 -> 49 0.14699
45 -> 51 0.19845
46 -> 50 -0.21737
47 -> 49 0.55286
48 -> 49 -0.17846
48 -> 52 0.16477

Excited State 10: Singlet-A 5.1097 eV 242.65 nm f=0.0438 <S**2>=0.000
45 -> 49 0.49605
46 -> 49 0.31093
46 -> 52 -0.19634
47 -> 51 0.21413
48 -> 50 0.22121

Excited State 11: Triplet-A 5.1505 eV 240.72 nm f=0.0000

<S**2>=2.000

44 -> 52	0.18392
45 -> 50	-0.12037
46 -> 50	0.44271
46 -> 51	0.23522
47 -> 49	-0.12817
47 -> 52	-0.14562
48 -> 52	-0.36630

Excited State 12: Triplet-A 5.1665 eV 239.98 nm f=0.0000
<S**2>=2.000

44 -> 50	0.14900
44 -> 51	0.13312
45 -> 49	-0.14086
45 -> 52	-0.17705
46 -> 52	0.42418
47 -> 50	-0.14379
47 -> 51	-0.17502
48 -> 50	-0.33023
48 -> 51	-0.25504

Excited State 13: Singlet-A 5.2157 eV 237.71 nm f=0.4550
<S**2>=0.000

45 -> 49	-0.32636
46 -> 49	0.59320
47 -> 50	0.10273
48 -> 51	-0.10355

Excited State 14: Triplet-A 5.2775 eV 234.93 nm f=0.0000
<S**2>=2.000

37 -> 49	0.16278
40 -> 49	0.30126
41 -> 49	-0.11864
43 -> 49	0.13880
44 -> 53	-0.13248
45 -> 51	-0.23389
46 -> 50	-0.21286
46 -> 51	0.31754
47 -> 52	-0.18635
47 -> 53	0.10194
48 -> 53	0.21004

Excited State 15: Singlet-A 5.4457 eV 227.67 nm f=0.0587
<S**2>=0.000

44 -> 49	-0.42695	
46 -> 51	-0.11074	
47 -> 49	0.23373	
48 -> 49	0.46791	

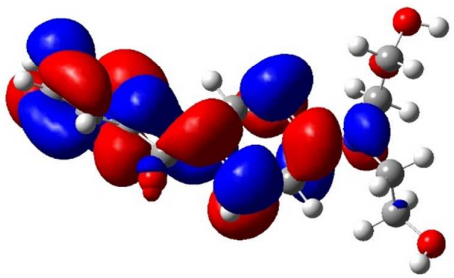
Excited State 16: Triplet-A 6.0360 eV 205.41 nm f=0.0000
<S**2>=2.000

38 -> 49	0.12454
46 -> 49	-0.33497
46 -> 53	-0.22660
47 -> 51	-0.14723
48 -> 50	0.38241
48 -> 51	-0.34325

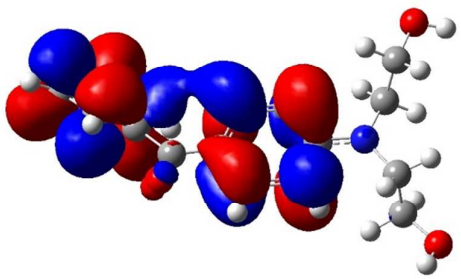
Excited State 17: Singlet-A 6.2646 eV 197.91 nm f=0.0391
<S**2>=0.000

45 -> 49	-0.34497
45 -> 52	0.10112
45 -> 53	-0.10566
46 -> 49	-0.13952
46 -> 52	-0.24189
47 -> 51	0.21684
48 -> 50	0.46141
48 -> 51	0.10291

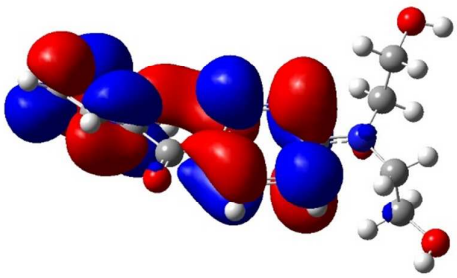
Figure S12. Excitation energies and oscillator strengths.



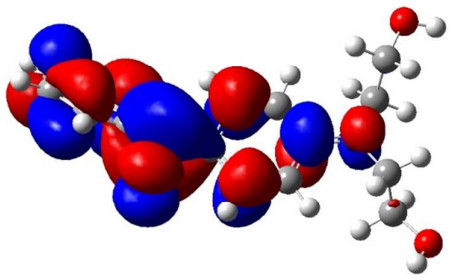
#80: C2 ~ symmetric (a) combination of benzene pi* (antibonding) MOs; descended from b1 in C2v. E = +0.04377



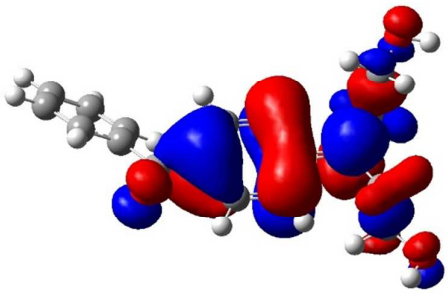
#79: C2 ~ symmetric (a) combination of benzene pi* antibonding MOs; descended from a2 in C2v. E = +0.04237



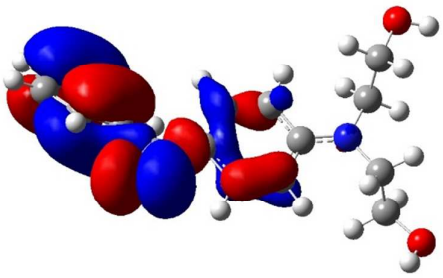
#78: ~a(2) Benzene pi*. E = 0.03240



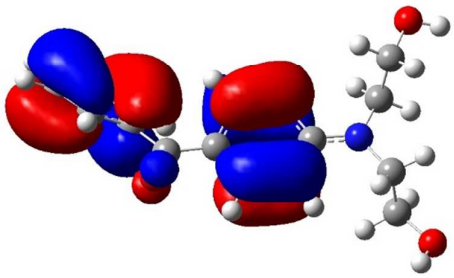
#77-LU: ~ b(1) pi* on CO with stabilizing admixture of benzene Lowest Unoccupied MO. E = -0.01239



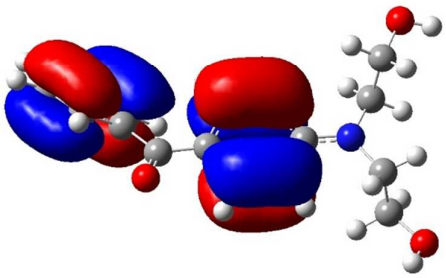
#76HO: local pi; benzene bonding pi elevated by N substituent N lone pair E = -0.25126



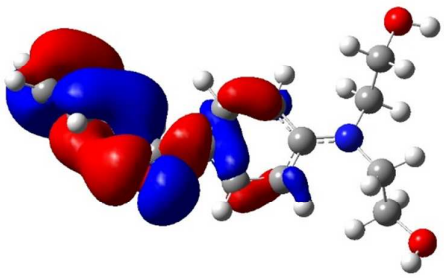
#75: O lone pair(once b2) mixed with U-benzene bonding MOs. E = -0.30688



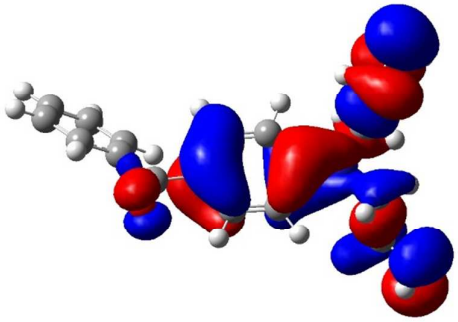
#74: a (2) combination of benzene pi bonding MOs. E = -0.31488



#73: a(2) combination of benzene pi bonding MOs.E = -0.31813



#72: O lone pair (~b2) mixed with U-benzene bonding MO E = =0.32142



#71: X-benzene stabilized by substituent. E = -0.33565

Figure S13. MOs and Absorption Spectrum of **K1**.

Excited State 1: Triplet-A 2.9490 eV 420.42 nm f=0.0000
<S**2>=2.000

71 -> 77	0.12557
75 -> 77	-0.19970
76 -> 77	0.54941
76 -> 78	-0.10165
76 -> 80	-0.27510

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -939.111500187
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 3.3837 eV 366.41 nm f=0.0000
<S**2>=2.000

72 -> 80	-0.14683
73 -> 79	0.15513
74 -> 77	0.15090
74 -> 78	0.17557
74 -> 79	-0.10035
75 -> 77	0.53268
75 -> 80	0.14536
76 -> 77	0.15130
76 -> 80	-0.10428

Excited State 3: Triplet-A 3.6179 eV 342.70 nm f=0.0000
<S**2>=2.000

72 -> 77	0.53437
73 -> 78	0.13620
73 -> 79	-0.12174

74 -> 77 -0.13020
74 -> 78 -0.14932
74 -> 79 0.13471
75 -> 77 0.15548
75 -> 79 -0.11443
75 -> 80 -0.15735
75 -> 84 0.10788

Excited State 4: Triplet-A 3.9859 eV 311.06 nm f=0.0000
<S**2>=2.000
76 -> 78 0.51917
76 -> 79 0.39418
76 -> 80 -0.20861

Excited State 5: Singlet-A 3.9932 eV 310.49 nm f=0.0380
<S**2>=0.000
72 -> 77 0.41986
75 -> 77 0.47581
76 -> 77 -0.23240

Excited State 6: Singlet-A 4.2863 eV 289.26 nm f=0.6456
<S**2>=0.000
71 -> 77 0.10530
75 -> 77 0.21340
76 -> 77 0.62975
76 -> 80 -0.14714

Excited State 7: Triplet-A 4.3190 eV 287.07 nm f=0.0000
<S**2>=2.000
73 -> 78 0.35661
73 -> 79 0.25510
73 -> 80 -0.19934
74 -> 78 0.25016
74 -> 79 0.23527
74 -> 80 -0.13928
76 -> 77 -0.23287

Excited State 8: Triplet-A 4.5000 eV 275.52 nm f=0.0000
<S**2>=2.000
72 -> 77 0.15288
73 -> 77 -0.35059
73 -> 80 -0.19805
74 -> 77 0.43162
74 -> 80 0.21601

75 -> 77 -0.14294
75 -> 80 -0.10422

Excited State 9: Triplet-A 4.6321 eV 267.67 nm f=0.0000
<S**2>=2.000
72 -> 77 0.26450
73 -> 78 -0.18839
73 -> 79 0.27804
74 -> 77 -0.13237
74 -> 78 0.26894
74 -> 79 -0.23825
75 -> 77 -0.20532
75 -> 78 -0.15636
75 -> 79 0.11981
76 -> 80 0.12184

Excited State 10: Singlet-A 4.7519 eV 260.92 nm f=0.0305
<S**2>=0.000
73 -> 77 -0.16959
73 -> 80 0.10805
74 -> 77 -0.17165
76 -> 78 0.49814
76 -> 79 0.35761
76 -> 80 -0.17711

Excited State 11: Triplet-A 4.8097 eV 257.78 nm f=0.0000
<S**2>=2.000
73 -> 77 0.47342
73 -> 80 -0.19909
74 -> 77 0.34158
74 -> 78 -0.11959
74 -> 80 -0.16556

Excited State 12: Triplet-A 4.9708 eV 249.43 nm f=0.0000
<S**2>=2.000
63 -> 77 -0.14406
69 -> 77 -0.18900
71 -> 77 0.16863
73 -> 78 0.17610
74 -> 79 0.16094
75 -> 80 0.10768
76 -> 77 0.14812
76 -> 78 0.12165
76 -> 80 0.40447

76 -> 84 0.17855
76 -> 85 0.13106

Excited State 13: Triplet-A 5.2088 eV 238.03 nm f=0.0000 <S**2>=2.000
72 -> 78 -0.24962
72 -> 79 0.26394
73 -> 77 0.10269
74 -> 77 -0.11567
74 -> 78 0.20635
74 -> 79 -0.24648
75 -> 78 0.33588
75 -> 79 -0.33521

Excited State 14: Singlet-A 5.2414 eV 236.55 nm f=0.0152 <S**2>=0.000
72 -> 77 0.15833
72 -> 78 0.13618
72 -> 79 -0.12802
73 -> 77 -0.34125
73 -> 80 -0.13307
74 -> 77 0.40754
74 -> 79 0.13192
74 -> 80 0.14886
75 -> 77 -0.15366
75 -> 78 -0.19294
75 -> 79 0.15847

Excited State 15: Singlet-A 5.5438 eV 223.65 nm f=0.1878 <S**2>=0.000
72 -> 77 0.48666
73 -> 77 0.11209
74 -> 77 -0.20679
75 -> 77 -0.38987

Excited State 16: Triplet-A 5.6450 eV 219.63 nm f=0.0000 <S**2>=2.000
58 -> 77 0.11544
63 -> 77 0.18797
69 -> 77 0.18482
71 -> 77 -0.18595
71 -> 80 0.11573
74 -> 80 -0.13847
75 -> 78 -0.11669

75 -> 80 -0.19461
76 -> 77 0.28196
76 -> 80 0.28587

Excited State 17: Singlet-A 5.7242 eV 216.60 nm f=0.1145 <S**2>=0.000
73 -> 77 0.40538
74 -> 77 0.34508
76 -> 78 0.31433
76 -> 79 0.10450
76 -> 80 0.25111

Excited State 18: Singlet-A 5.7788 eV 214.55 nm f=0.0882 <S**2>=0.000
73 -> 77 -0.27243
74 -> 77 -0.18755
76 -> 77 0.12469
76 -> 80 0.56374

Excited State 19: Triplet-A 6.1171 eV 202.68 nm f=0.0000 <S**2>=2.000
63 -> 77 0.14790
69 -> 77 -0.20783
69 -> 80 0.16091
71 -> 77 0.33012
71 -> 80 -0.18770
72 -> 77 -0.16358
72 -> 80 0.17658
75 -> 80 -0.17445

Excited State 20: Triplet-A 6.1864 eV 200.41 nm f=0.0000 <S**2>=2.000
76 -> 78 -0.39772
76 -> 79 0.54384

Excited State 21: Singlet-A 6.2039 eV 199.85 nm f=0.0032 <S**2>=0.000
76 -> 78 -0.35964
76 -> 79 0.57751

Excited State 22: Triplet-A 6.4080 eV 193.48 nm f=0.0000 <S**2>=2.000
64 -> 77 -0.14800
72 -> 77 0.11967

72 -> 78 0.29038
72 -> 80 0.28743
75 -> 78 0.30003
75 -> 79 0.13083
75 -> 80 0.34563

Excited State 23: Singlet-A 6.4357 eV 192.65 nm f=0.1091 <S**2>=0.000
72 -> 79 0.10381
73 -> 77 -0.23908
73 -> 80 0.10455
74 -> 77 0.24811
74 -> 79 -0.15231
75 -> 78 0.46783
75 -> 79 -0.21613
75 -> 80 0.10384

Excited State 24: Triplet-A 6.4783 eV 191.38 nm f=0.0000 <S**2>=2.000
70 -> 82 -0.13314
71 -> 81 -0.13529
76 -> 81 0.63941

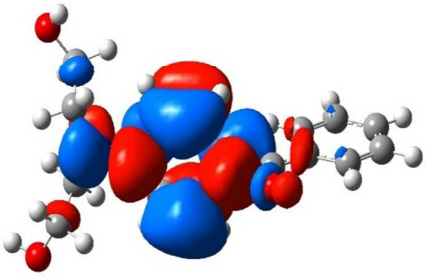
Excited State 25: Singlet-A 6.5806 eV 188.41 nm f=0.1156 <S**2>=0.000
72 -> 78 0.20193
72 -> 80 0.15113
73 -> 78 -0.11872
73 -> 79 0.15305
74 -> 77 -0.10981
74 -> 78 0.24719
74 -> 80 0.12254
75 -> 79 0.28221
75 -> 80 0.41660

Excited State 26: Singlet-A 6.6242 eV 187.17 nm f=0.0151 <S**2>=0.000
76 -> 81 0.66038
76 -> 85 -0.10374

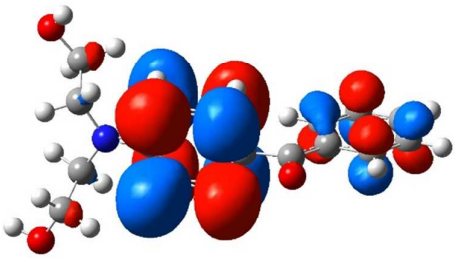
Excited State 27: Singlet-A 6.6399 eV 186.73 nm f=0.3803 <S**2>=0.000
69 -> 77 0.10243
71 -> 77 -0.21123

```
        72 -> 78        0.30108
        73 -> 79       -0.24119
        74 -> 78       -0.30902
        75 -> 78        0.31392
        75 -> 79        0.15240

 Excited State   28:      Triplet-A      6.6508 eV  186.42 nm  f=0.0000
<S**2>=2.000
        72 -> 78        0.36331
        72 -> 80       -0.25580
        74 -> 80       -0.10557
        75 -> 78        0.33598
        75 -> 80       -0.30317

 Excited State   29:      Triplet-A      6.7128 eV  184.70 nm  f=0.0000
<S**2>=2.000
        72 -> 79        0.13420
        73 -> 77        0.21958
        73 -> 78       -0.11218
        73 -> 79       -0.10694
        73 -> 80       -0.28174
        73 -> 84        0.10174
        74 -> 77       -0.18988
        74 -> 78        0.13864
        74 -> 79        0.14596
        74 -> 80        0.32731
        74 -> 84       -0.12450
        75 -> 79        0.11730
        75 -> 80       -0.13015

 Excited State   30:      Singlet-A      6.7186 eV  184.54 nm  f=0.0279
<S**2>=0.000
        69 -> 77       -0.20539
        71 -> 77        0.42556
        71 -> 80       -0.11230
        72 -> 78        0.17965
        72 -> 80        0.16433
        73 -> 78        0.18792
        74 -> 78       -0.13271
        74 -> 79        0.21401
        75 -> 79       -0.12220
```

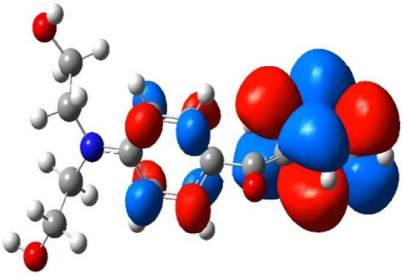
Figure S14. Excitation energies and oscillator strengths.



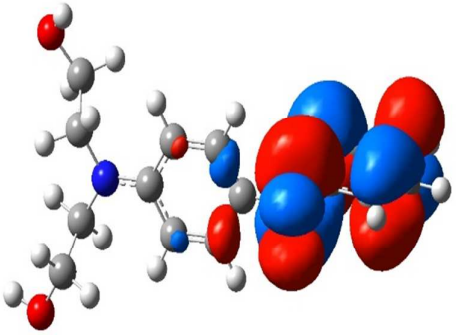
#52: O lone pair with X-benzene pi* (antibonding) MO;. E = +0.05643



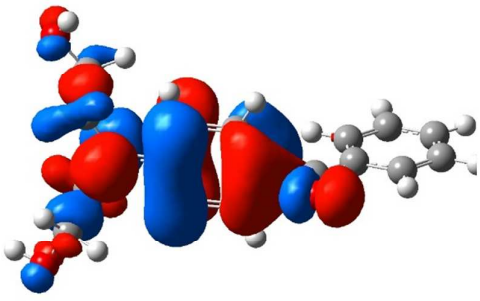
#79: X- benzene pi* antibonding MO; E = +0.04443

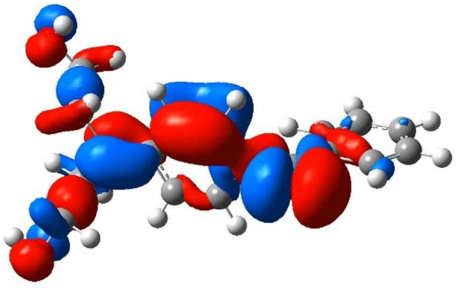


#78: U-benzene pi*. E = 0.02870

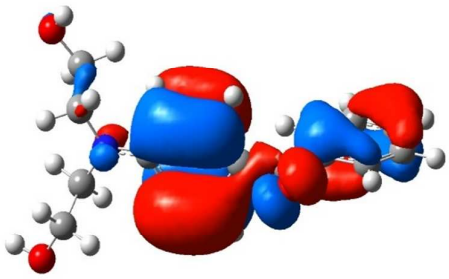


#77: pi* on CO with stabilizing admixture of U-benzene * Lowest Unoccupied MO. E = -0.03462

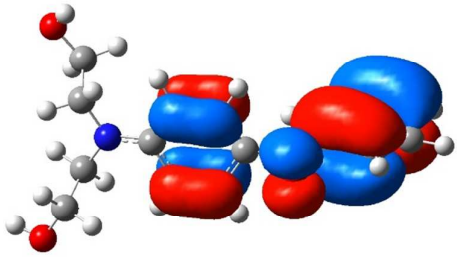




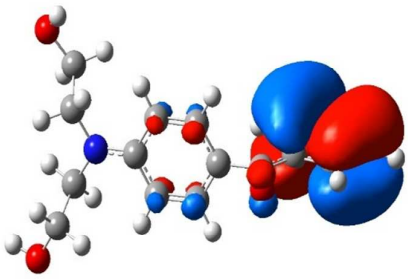
#76 small amplitude of O lone pair (pseudo-pi) with more N lone pair destabilizing admixture from a X-benzene pi bonding MO. E = -0.23269



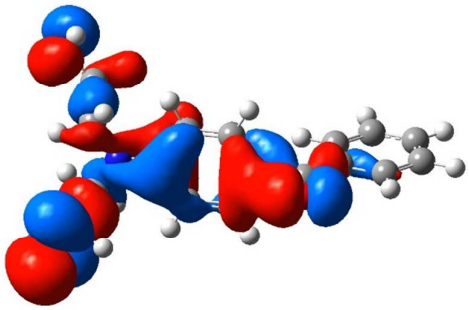
#75: N lone pair and O lone pair (pseudo-pi) E = -0.30740



#74: mostly X-benzene pi bonding MOs. E = -0.30940

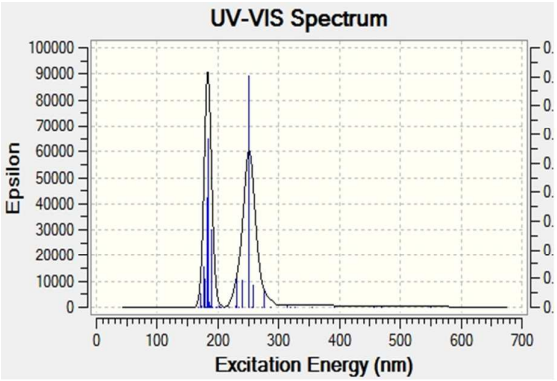


#73: combination of benzene pi bonding MOs. E = -0.31950



#72: pi bonding on U-benzene. E = -0.32541

#71: E = -0.34505



Triplet 75 and 76 to 77 at 550 nm (2.26 eV) nπ*
Triplet 75 and 76 at 470 nm (2.64 eV) nπ*
Triplet 73 to 77 at 456 nm (2.72 eV) ππ*
Triplet 76 to 80 at 392 nm (3.171 eV) ππ*
Triplet 76 to 79 at 326 nm (3.80 eV) ππ*-benz
Triplet 72 to 77 at 319 nm (3.88 eV)
Singlet 75 and 76 to 77 at 314 nm (3.95 eV) weak = 0.0029
Triplet 72 to 78 at 288 nm (4.31 eV)
Singlet 76 to 79 at 276 nm (4.48 eV) med = 0.0563
Triplet 74 to 79 at 273 nm (4.55 eV)
Singlet 72 to 77 at 258 nm (4.80 eV) med = 0.0746
Singlet mixed at 251 nm (4.93 eV) strong 0.8025

Figure S15. MOs and Spectrum for S_1 of **K1**.

Excited State 1: Triplet-A 2.2555 eV 549.70 nm f=0.0000 <S**2>=2.000
71 -> 77 -0.12929
74 -> 77 0.12823
75 -> 77 0.41324
75 -> 82 -0.14451
76 -> 77 0.49493
76 -> 82 -0.11295
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -939.111661023
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.6398 eV 469.67 nm f=0.0012 <S**2>=0.000
75 -> 77 0.34757
75 -> 82 -0.10754
76 -> 77 0.57486
76 -> 82 -0.10860

Excited State 3: Triplet-A 2.7166 eV 456.40 nm f=0.0000 <S**2>=2.000
64 -> 77 -0.10765
64 -> 82 0.12411
72 -> 77 -0.13290
72 -> 78 0.20909

73 -> 77 0.56166
74 -> 77 -0.30750
73 <- 77 0.12667

Excited State 4: Triplet-A 3.1664 eV 391.57 nm f=0.0000
<S**2>=2.000
71 -> 80 0.11594
74 -> 79 -0.21952
76 -> 80 0.63388
76 <- 80 0.11406

Excited State 5: Triplet-A 3.4797 eV 356.31 nm f=0.0000
<S**2>=2.000
71 -> 77 0.12413
75 -> 77 -0.18924
76 -> 77 0.21724
76 -> 78 0.21242
76 -> 79 0.56964

Excited State 6: Triplet-A 3.7992 eV 326.34 nm f=0.0000
<S**2>=2.000
69 -> 77 -0.13167
71 -> 77 0.21601
75 -> 77 -0.32413
76 -> 77 0.41864
76 -> 78 -0.13563
76 -> 79 -0.30089

Excited State 7: Triplet-A 3.8851 eV 319.13 nm f=0.0000
<S**2>=2.000
72 -> 77 0.66068
72 -> 82 0.11008
73 -> 77 0.18981

Excited State 8: Singlet-A 3.9537 eV 313.59 nm f=0.0029
<S**2>=0.000
69 -> 77 0.14183
71 -> 77 -0.26271
74 -> 77 0.13437
75 -> 77 0.46215
75 -> 82 -0.11707
76 -> 77 -0.37345

Excited State 9: Triplet-A 4.3099 eV 287.67 nm f=0.0000

<S**2>=2.000

58 -> 77	0.10021
64 -> 77	0.25182
68 -> 77	-0.12824
72 -> 78	0.50602
72 -> 79	-0.14642
73 -> 78	0.18339
73 -> 82	0.15451
74 -> 77	0.11409

Excited State 10: Singlet-A 4.4850 eV 276.44 nm f=0.0563
<S**2>=0.000

74 -> 80	0.14938
76 -> 78	0.28855
76 -> 79	0.61623

Excited State 11: Triplet-A 4.5463 eV 272.72 nm f=0.0000
<S**2>=2.000

73 -> 79	0.22228
74 -> 77	0.14747
74 -> 78	0.18079
74 -> 79	0.50955
75 -> 79	-0.15729
76 -> 80	0.26994

Excited State 12: Singlet-A 4.8045 eV 258.06 nm f=0.0746
<S**2>=0.000

72 -> 77	0.58129
73 -> 77	0.29903
73 -> 78	-0.20577
74 -> 78	0.11070

Excited State 13: Triplet-A 4.8245 eV 256.99 nm f=0.0000
<S**2>=2.000

64 -> 77	0.39336
66 -> 77	0.13483
67 -> 77	-0.10056
68 -> 77	-0.19168
72 -> 78	-0.32274
72 -> 79	0.10170
73 -> 77	0.21668
73 -> 78	-0.12949
73 -> 82	0.18942
74 -> 82	-0.11673

Excited State 14: Singlet-A 4.9311 eV 251.43 nm f=0.8025 <S**2>=0.000

72 -> 77	0.20950
73 -> 77	-0.37246
74 -> 77	0.36417
76 -> 80	0.39481

Figure S16. Excitation energies and oscillator strengths.

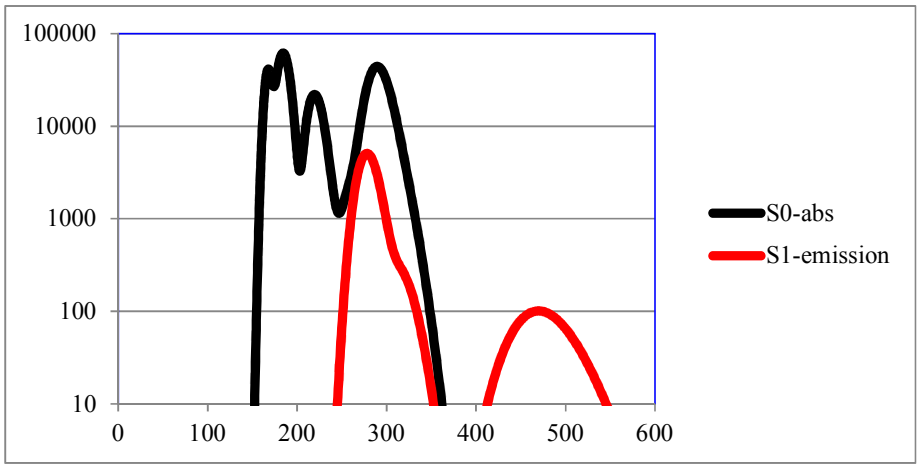


Figure S17. The computed absorption and emission spectrum of **K1**.

References

(1) Parker, C. A.; Rees, W. T. Correction of Fluorescence Spectra and Measurement of Fluorescence Quantum Efficiency. *Analyst.* **1960,** *85,* 587-600.

(2) ASTM D2572-97, Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers. ASTM International, West Conshohocken, PA. http://www.astm.org. **2010**.