Supporting information

Self-enhanced solid state electrochemiluminescence sensing platform SiO_2-PEI NPs and its application in the detection of spermine

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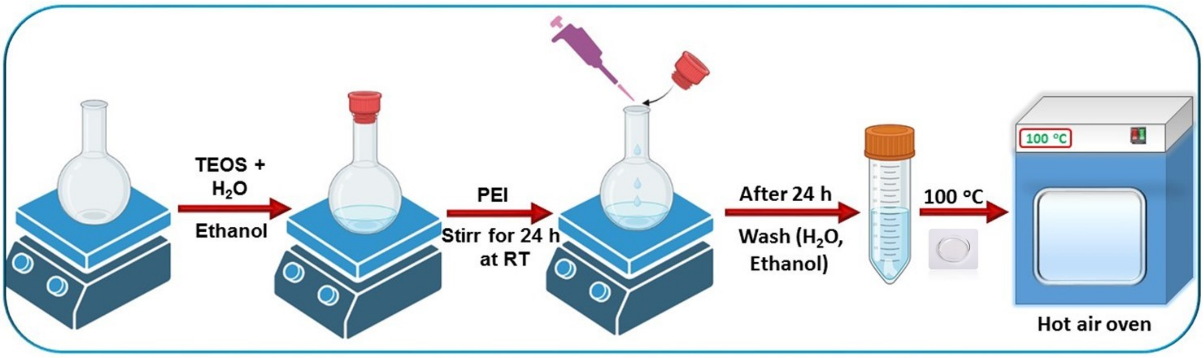
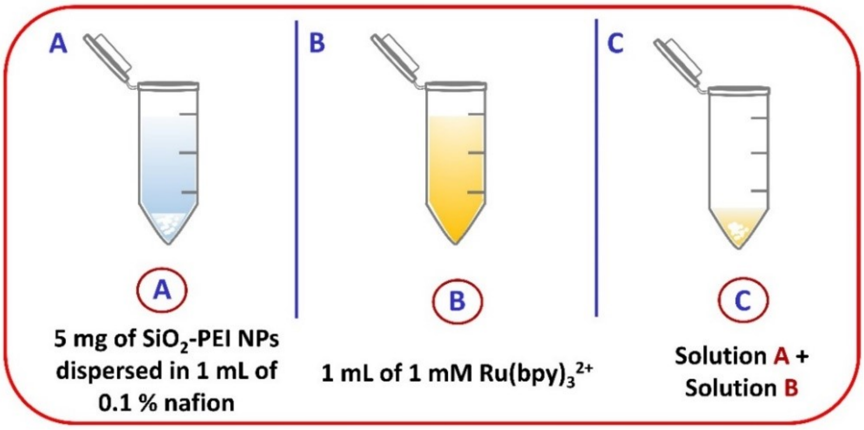
Schematic representation for the synthesis of SiO_2-PEI NPs using stöber method



Scheme S1. *Schematic representation showing synthesis of SiO_2 NPs & SiO_2-PEI NPs via stÖber method;*

Schematic representation of ink preparation for modifying GCE surface



Scheme S2. *Steps involved in the ink preparation of SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE surface.*

Control experiments

The CV and ECL intensity curves for $[Ru(bpy)_3]^{2+}$/Nf and SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE. As shown in the figure S2, the results suggest that the most effective enhancement in the ECL emission intensity was observed for the SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE. Therefore, we have chosen SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE for ECL experiments in the detection of spermine molecule. Also, in the case of SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE, PEI NPs in the SiO_2 PEI NPs matrix will act as a co-reactant accelerator, which plays crucial role in stabilizing the developed solid-state ECL sensing platform.

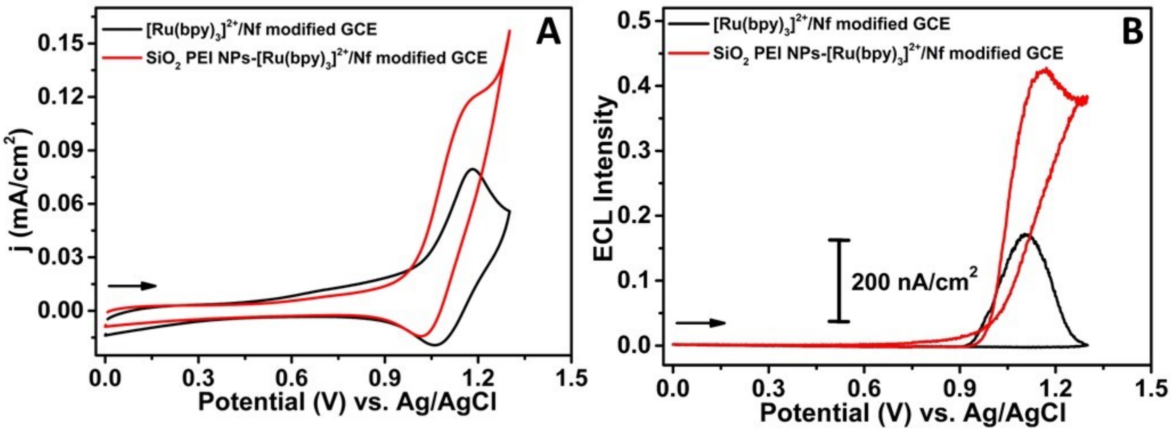


Figure S1. *CV and ECL emission intensity plot of $[Ru(bpy)_3]^{2+}$/Nf modified GCE* (black); and *SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE (red) surface under N_2-saturated 0.1 M PBS electrolyte, with the scan rate of 50 mV/s.*

Effect of pH

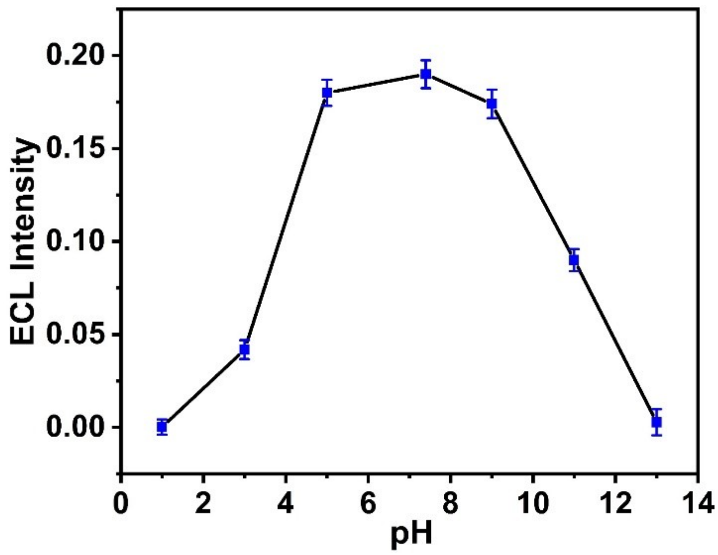


Figure S2. *Derivative plot of ECL emission intensity recorded at a SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE surface under N_2-saturated 0.1 M PBS electrolyte, with the scan rate of 50 mV/s.*

The influence of pH on ECL emission intensity was also studied at a constant concentration of SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE under N_2 saturated 0.1 M PBS (pH 7.4) under cyclic voltammetric conditions, as shown in the Figure S2. The ECL of of SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE is highly dependent on pH of the electrolyte solution. As seen from the Figure S1, the ECL emission diminishes in the pH > 7.4 and however, at pH greater than 7.4, the ECL emission decreases gradually. Therefore, the physiological pH value 7.4 was chosen as the optimum pH for all the experimental work.

Effect of Scan rate

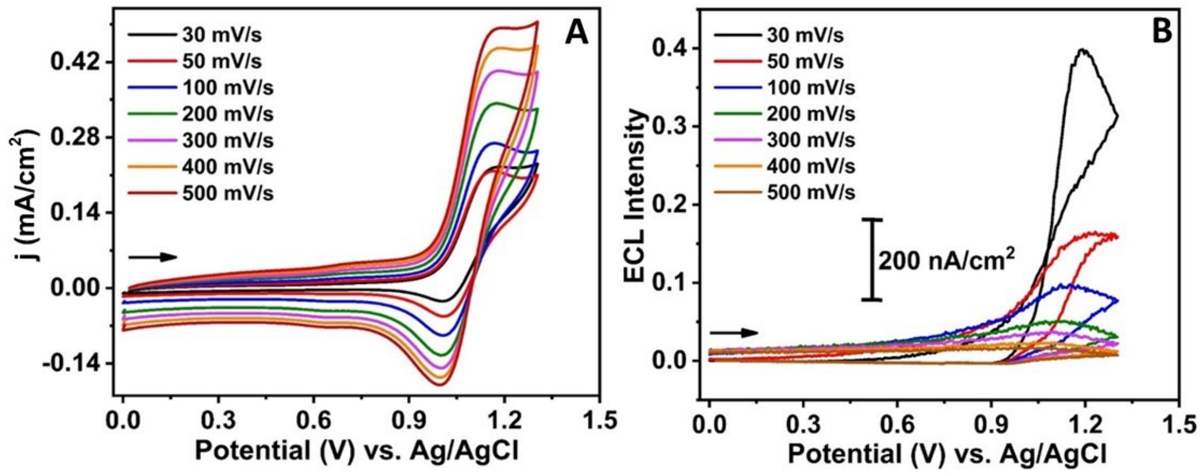


Figure S3. *Shows the simultaneously recorded CV (A) and their ECL emission signals (B) in N_2 0.1 M PBS (pH 7.4) electrolyte at a SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE surface under N_2-saturated 0.1 M PBS electrolyte, at different scan rates.*

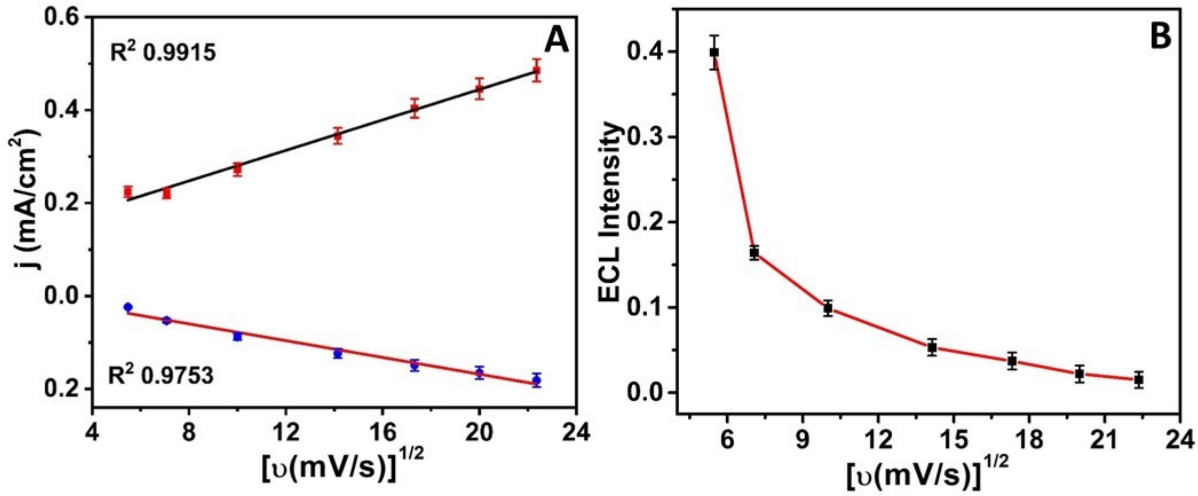


Figure S4. *Linear plot for CV and their corresponding ECL signals recorded at a SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE surface under N_2-saturated 0.1 M PBS electrolyte, at different scan rates.*

ECL quenching mechanism in O_2 atmosphere

The ECL quenching mechanism behind the $[Ru(bpy)_3]^{2+}$ chemically modified SiO_2 PEI matrix in the presence of dissolved oxygen (O_2) in the 0.1 M PBS electrolyte solution in the revised manuscript. Here, the formed $[Ru(bpy)_3]^{+}$ reacts with the O_2 present in the electrolyte solution, which chemically produces the $[Ru(bpy)_3]^{2+}$, without the formation of excited state $[Ru(bpy)_3]^{2+*}$ [1, 2].

$$\mathrm{PEI} \xrightarrow{-e^-} \mathrm{PEI}^{\bullet +}$$

PEI in the SiO_2PEI matrix **$PEI^{\bullet +}$ cation radical**

$$\mathrm{PEI}^{\bullet +} \xrightarrow{-H^+} \mathrm{PEI}^{\bullet}$$

$PEI^{\bullet +}$ cation radical **$PEI^{\bullet}$ radical**

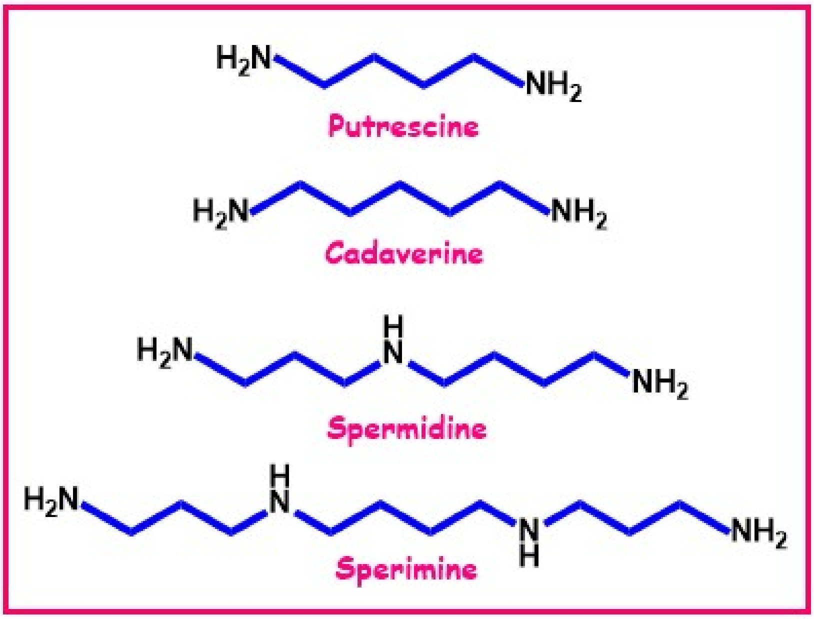
$$\mathrm{PEI}^{\bullet} + O_2 \longrightarrow \mathrm{PEI}^{+} + \mathrm{P1}$$

$PEI^{\bullet}$ radical

$$[\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{PEI}^{\bullet} \longrightarrow [\mathrm{Ru(bpy)_3}]^{+} + \mathrm{P2}$$

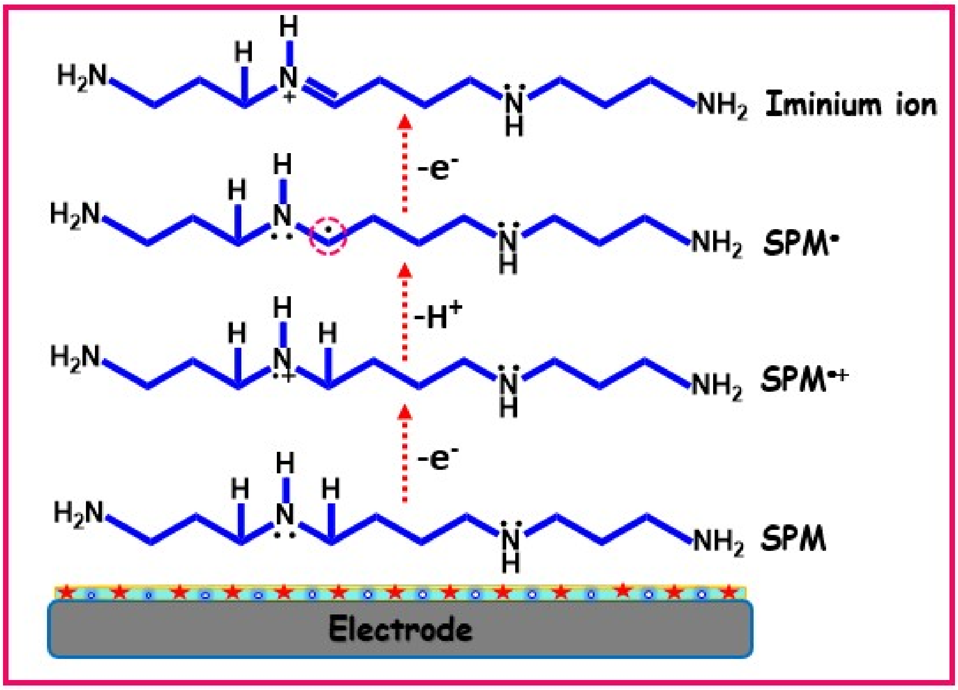
$$[\mathrm{Ru(bpy)_3}]^{+} + O_2 \longrightarrow [\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{P3}$$

Chemical structure of spermine, spermidine, putrescine, and cadaverine



Scheme S3. *Schematic representation showing the chemical structure of the biogenic amines such as putrescine, cadaverine, spermidine, and spermine.*

Oxidation reaction sequence of Spermine on the SiO_2-PEI NPs/$[Ru(bpy)_3]^{2+}$/Nafion modified GCE electrode surface



Scheme S4. *Proposed schematic representation showing spermine (SPM) oxidation reaction sequence a SiO_2 PEI NPs-$[Ru(bpy)_3]^{2+}$/Nf modified GCE surface under N_2-saturated 0.1 M PBS electrolyte at with its abbreviations.*

XPS survey spectrum of SiO_2 NPs and SiO_2-PEI NPs

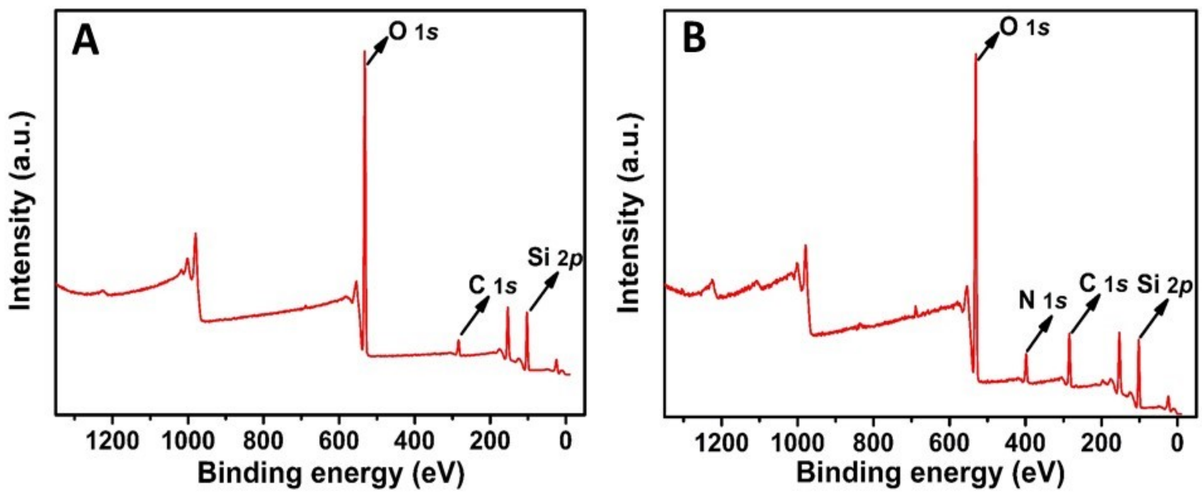
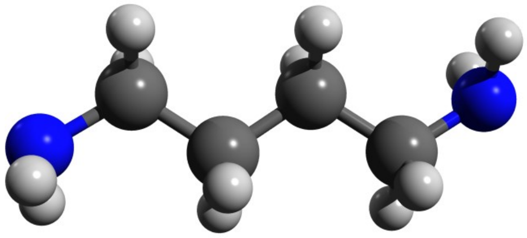


Figure S4. *X-ray photoelectron spectroscopy (XPS) (a) survey spectrum of SiO_2 NPs; (b) survey spectrum of SiO_2 PEI NPs.*

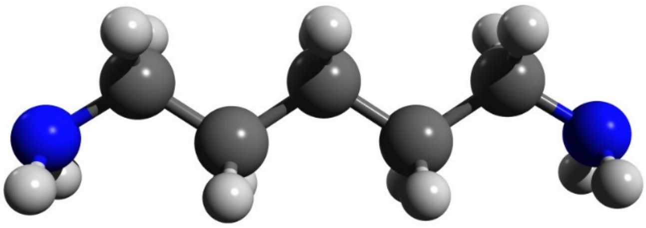
Geometric optimization of spermine, spermidine, putrescine, and cadaverine using DFT

Table S1: Optimized geometry (B3LYP-D4/TZVP level)

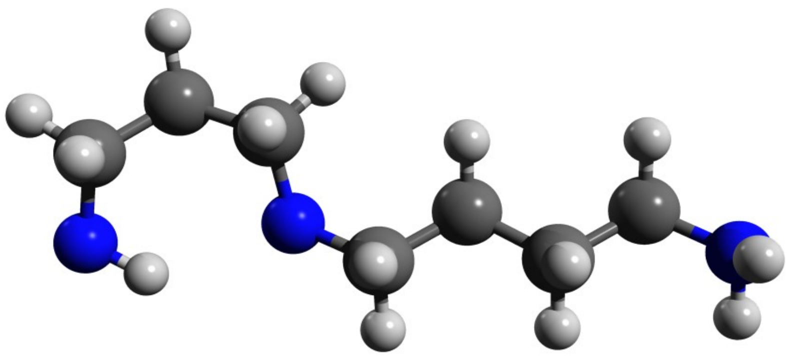
Putrascine



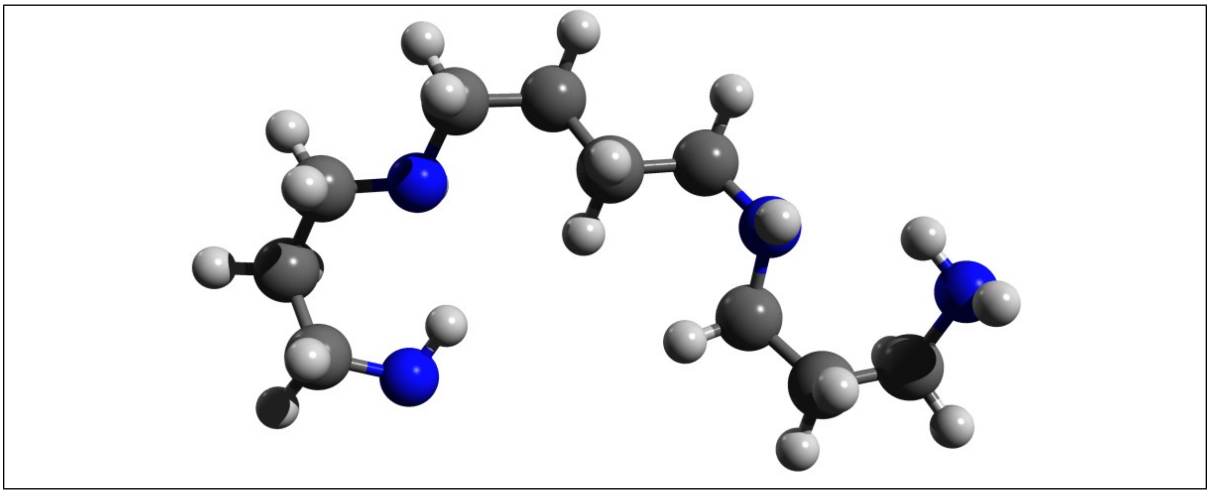
Cadavarine



Spermidine

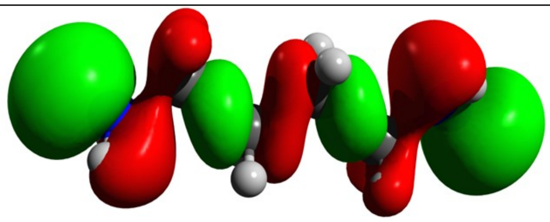
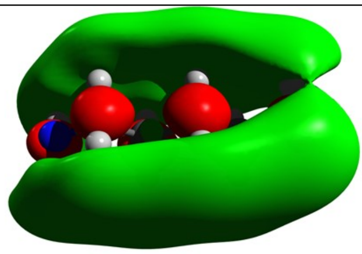
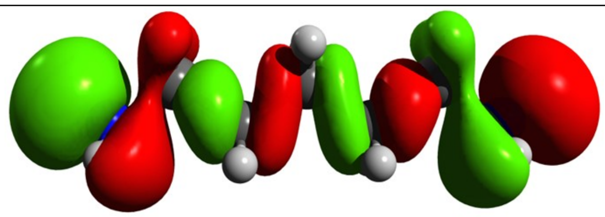
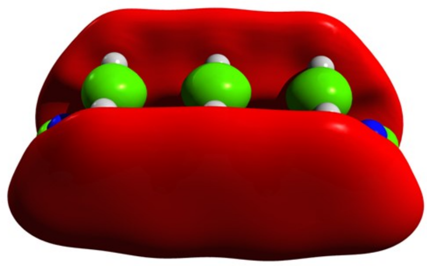


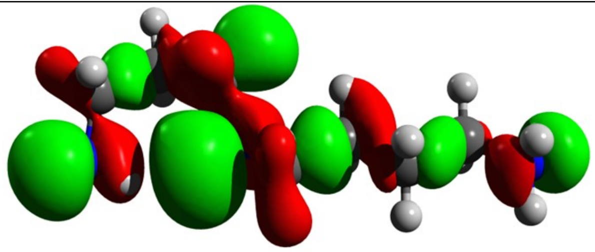
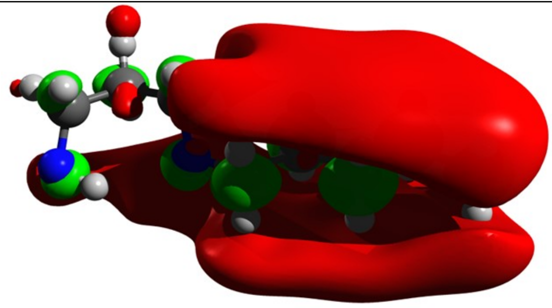
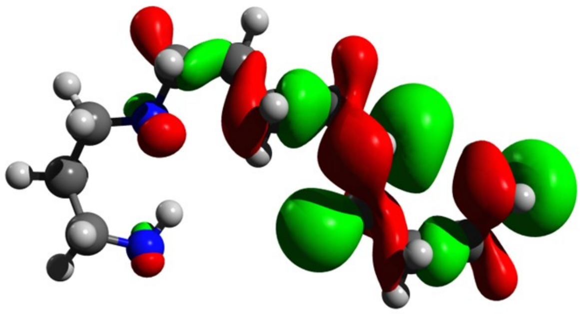
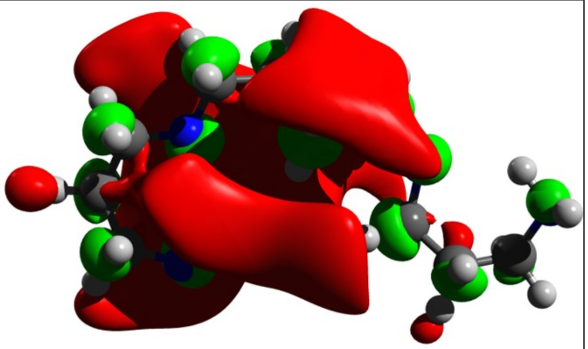
Spermine



Images generated with Avogadro and POV-Ray [3, 4].

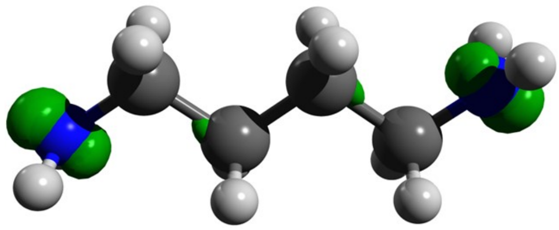
HOMO/LUMO of spermine, spermidine, putrescine, and cadaverine

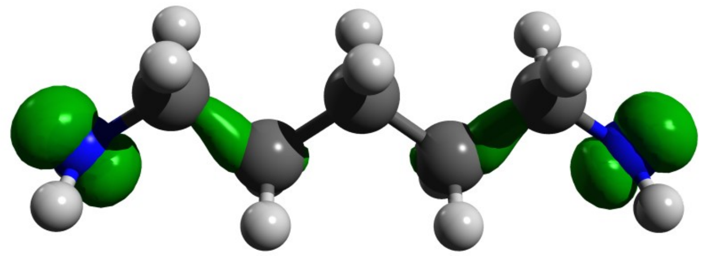
Table S2: HOMO/LUMO of molecules [isovalue = 0.02]	
Putrascine	
 HOMO (-6.339 eV)	 LUMO (1.077 eV)
Cadavarine	
 HOMO (-6.371 eV)	 LUMO (1.056 eV)
Spermidine	

 HOMO (-5.805 eV)	 LUMO (1.188 eV)
Spermine	
 HOMO (-5.821 eV)	 LUMO (0.998 eV)

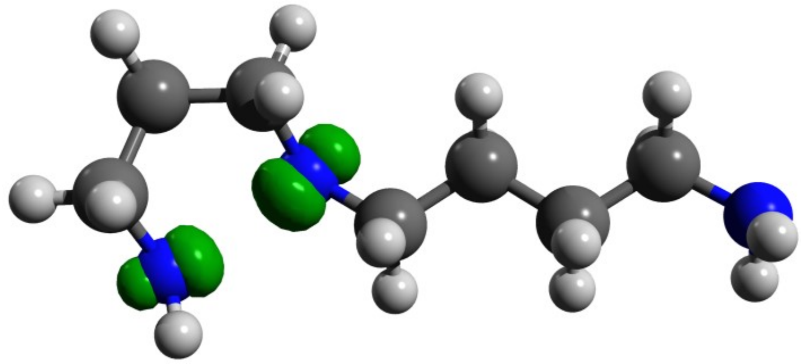
Images generated with Avogadro and POV-Ray.

Spin density data and plots for spermine, spermidine, putrescine, and cadaverine

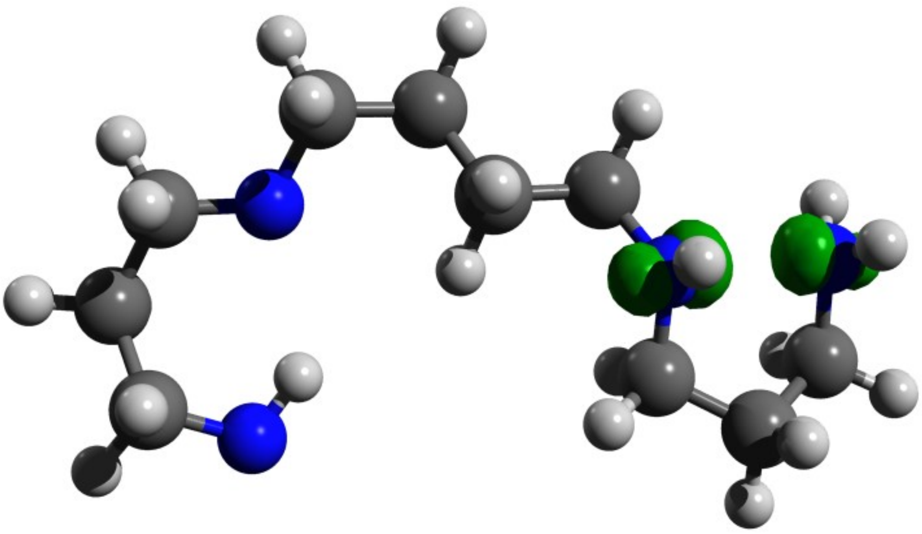
Table S3: Spin density plots (Isovalue = 0.02)
Putrascine (+1 charged) 
Cadavarine (+1 charged)



Spermidine (+1 charged)



Spermine (+1 charged)



Images generated with Avogadro and POV-Ray.

Atomic charges and spin populations for spermine, spermidine, putrescine, and cadaverine

Table S4: Atomic charges and spin populations for molecules

Putrascine

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
   0 N :    0.049580    0.361823
   1 C :   -0.286485    0.051451
   2 H :    0.146886    0.003586
   3 H :    0.146880    0.003573
   4 C :   -0.227772    0.070978
   5 H :    0.148629    0.000136
   6 H :    0.148626    0.000135
   7 C :   -0.227778    0.070973
   8 H :    0.148623    0.000135
   9 H :    0.148627    0.000137
  10 C :   -0.286498    0.051445
  11 H :    0.146880    0.003581
  12 H :    0.146878    0.003578
  13 N :    0.049532    0.361750
  14 H :    0.186846    0.004179
  15 H :    0.186845    0.004179
  16 H :    0.186849    0.004180
  17 H :    0.186852    0.004181
```

Cadaverine

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
   0 C :   -0.289800    0.050082
   1 C :   -0.230989    0.069050
   2 H :    0.145824   -0.000198
   3 H :    0.145814   -0.000206
   4 C :   -0.235820    0.033434
   5 H :    0.146044   -0.000176
   6 H :    0.146046   -0.000176
   7 C :   -0.230944    0.069106
   8 H :    0.145816   -0.000205
   9 H :    0.145823   -0.000196
  10 C :   -0.289787    0.050140
  11 H :    0.145723    0.004081
  12 H :    0.145712    0.004062
  13 N :    0.039347    0.348421
  14 H :    0.185196    0.004137
```

```
 15 H :    0.185189    0.004139
 16 N :    0.039091    0.348110
 17 H :    0.145693    0.004058
 18 H :    0.145701    0.004067
 19 H :    0.185162    0.004134
 20 H :    0.185159    0.004134
```

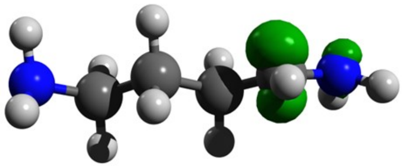
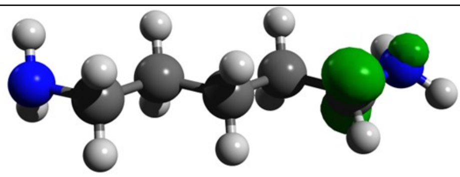
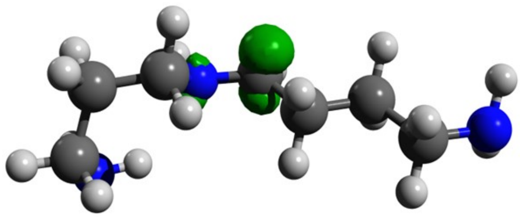
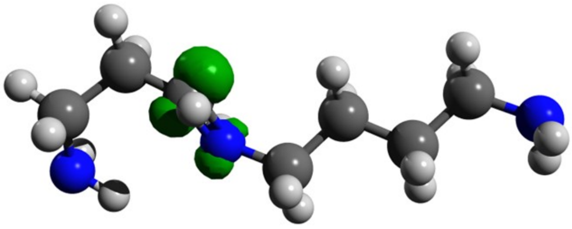
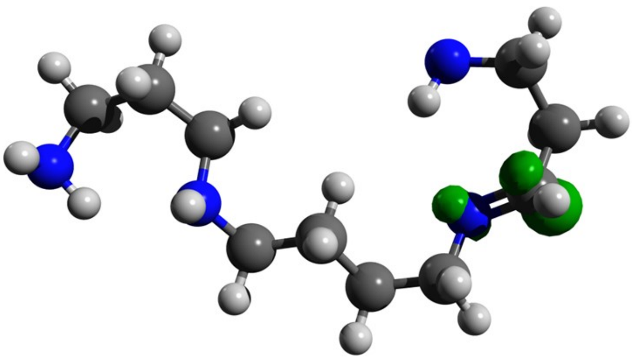
Spermidine

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
  0 H :    0.140637    0.000922
  1 H :    0.147111   -0.000309
  2 C :   -0.254941    0.046944
  3 C :   -0.306711    0.031435
  4 C :   -0.244784    0.037424
  5 N :   -0.037002    0.243320
  6 H :    0.145854    0.008746
  7 H :    0.154177   -0.000395
  8 C :   -0.335234    0.009255
  9 C :   -0.261127    0.013802
 10 H :    0.138126    0.000427
 11 H :    0.138072   -0.000006
 12 C :   -0.240379    0.044926
 13 H :    0.144788    0.000810
 14 H :    0.144996   -0.000242
 15 C :   -0.263651    0.039499
 16 H :    0.151829    0.006843
 17 H :    0.149889    0.002216
 18 N :    0.197308    0.420421
 19 H :    0.214051    0.004775
 20 H :    0.172583    0.044350
 21 H :    0.166476    0.003327
 22 H :    0.176771    0.002547
 23 H :    0.130934    0.000137
 24 H :    0.130963    0.000127
 25 N :   -0.169567    0.033936
 26 H :    0.156974    0.000354
 27 H :    0.157186    0.000392
 28 H :    0.154668    0.004019
```

Spermine

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
  0 H :    0.128236    0.000218
  1 H :    0.134605   -0.000033
  2 C :   -0.304059    0.005745
  3 C :   -0.343595    0.004861
```

4 C :	-0.271276	0.004725
5 N :	-0.172582	0.042532
6 H :	0.127944	0.001111
7 H :	0.139916	0.000141
8 C :	-0.270539	0.033063
9 C :	-0.246921	0.036998
10 H :	0.139859	0.000322
11 H :	0.143340	-0.000301
12 C :	-0.251669	0.008689
13 H :	0.143585	0.000069
14 H :	0.141313	-0.000068
15 C :	-0.297284	0.014648
16 H :	0.136225	0.001426
17 H :	0.130608	0.011864
18 N :	0.016659	0.063973
19 H :	0.181845	0.000711
20 H :	0.124311	0.005972
21 H :	0.144185	0.000511
22 H :	0.153493	0.000322
23 H :	0.148053	0.005119
24 H :	0.147588	0.002310
25 N :	0.174055	0.375513
26 H :	0.135532	0.001006
27 H :	0.173460	0.002246
28 H :	0.152081	-0.000372
29 H :	0.143386	0.007784
30 N :	-0.056316	0.215940
31 C :	-0.311490	0.027883
32 C :	-0.248536	0.033149
33 C :	-0.261090	0.041674
34 H :	0.163862	0.003013
35 H :	0.145328	-0.000281
36 H :	0.138853	0.000816
37 H :	0.209416	0.004391
38 H :	0.165531	0.038753
39 H :	0.152088	0.003555

Table S5: Spin density plots for carbon radicals (Isovalue = 0.02)	Radical stabilization energy (Kcal/mol)
Putrascine	
	13.44913
Cadavarine	
	13.45222
Spermidine	
Radical 1 	14.70367
Radical 2 	17.00095
Spermine	
Radical 1 	16.26578

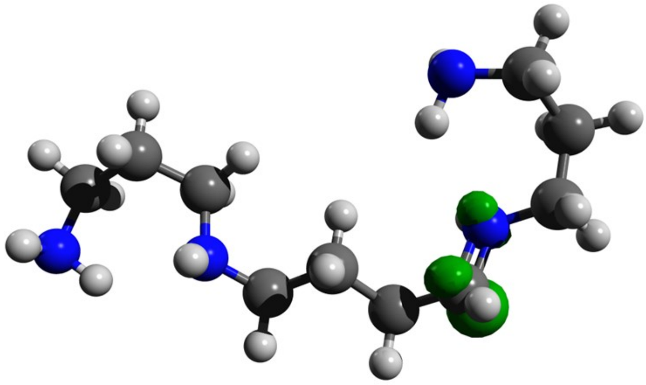
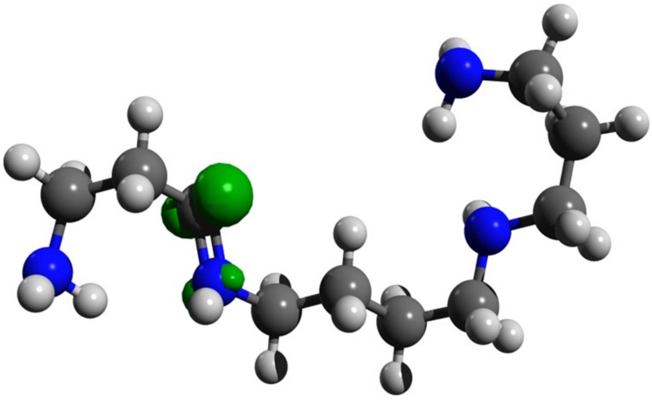
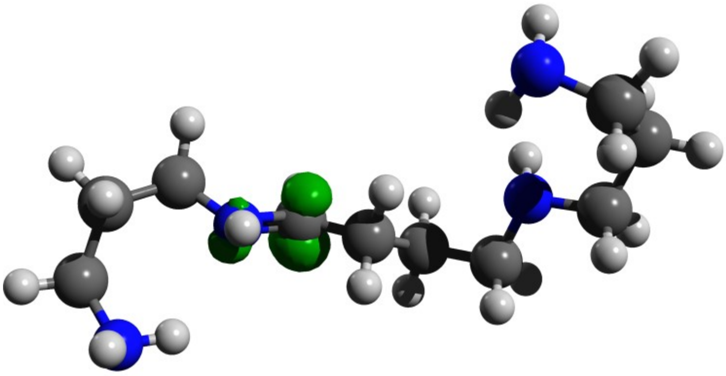
Radical 2 	15.14198
Radical 3 	16.9253
Radical 4 	14.77138

Table S6: ATOMIC CHARGES AND SPIN POPULATIONS
Putrascine
---   LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS   ---   0 N : -0.192173 0.063899   1 C : -0.234932 0.785333   2 H : 0.119289 0.007492   3 C : -0.288238 0.063033

```
  4 H :   0.136001    0.005920
  5 H :   0.141873    0.033020
  6 C :  -0.279996    0.002561
  7 H :   0.132223   -0.000198
  8 H :   0.131905    0.001114
  9 C :  -0.340725    0.000413
 10 H :   0.126941    0.000025
 11 H :   0.126849    0.000511
 12 N :  -0.201934   -0.000067
 13 H :   0.152572    0.000047
 14 H :   0.152531    0.000003
 15 H :   0.162486    0.034139
 16 H :   0.155327    0.002758
```

Cadavarine

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
  0 C :  -0.235144    0.785240
  1 C :  -0.289281    0.063125
  2 H :   0.135517    0.005923
  3 H :   0.141446    0.033172
  4 C :  -0.264314    0.002433
  5 H :   0.135076   -0.000192
  6 H :   0.134731    0.001155
  7 C :  -0.279663    0.000388
  8 H :   0.131649    0.000041
  9 H :   0.131552    0.000486
 10 C :  -0.340318    0.000013
 11 H :   0.126487    0.000011
 12 H :   0.126523    0.000054
 13 N :  -0.202838   -0.000094
 14 H :   0.152335    0.000010
 15 H :   0.152348   -0.000002
 16 N :  -0.192717    0.063811
 17 H :   0.119010    0.007563
 18 H :   0.155240    0.002742
 19 H :   0.162362    0.034120
```

Spermidine

Radical 1

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
  0 H :   0.126025    0.000042
  1 H :   0.133365    0.000270
  2 C :  -0.309312    0.008869
```

```
  3 C :   -0.340261    0.000206
  4 C :   -0.279594    0.001571
  5 N :   -0.211262    0.000037
  6 H :    0.126307    0.000032
  7 H :    0.140741   -0.000148
  8 C :   -0.341120    0.000442
  9 C :   -0.279461    0.002372
 10 H :    0.132159   -0.000215
 11 H :    0.132338    0.001106
 12 C :   -0.279177    0.062941
 13 H :    0.136689    0.005820
 14 H :    0.143226    0.032755
 15 C :   -0.204458    0.779184
 16 H :    0.121460    0.006420
 17 N :   -0.020835    0.063493
 18 H :    0.180253    0.030603
 19 H :    0.119091    0.001551
 20 H :    0.136215   -0.000109
 21 H :    0.149800    0.000020
 22 H :    0.126950    0.000030
 23 H :    0.126850    0.000512
 24 N :   -0.201977   -0.000075
 25 H :    0.152515    0.000005
 26 H :    0.152712    0.000045
 27 H :    0.130761    0.002220
```

Radical 2

```
-------------------------------------------
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
-------------------------------------------
  0 H :    0.125535    0.001546
  1 H :    0.140859    0.031351
  2 C :   -0.209066    0.759342
  3 C :   -0.340627    0.009297
  4 C :   -0.294565    0.049170
  5 N :   -0.209936    0.001624
  6 H :    0.126620    0.000497
  7 H :    0.141168    0.001758
  8 C :   -0.340754    0.000069
  9 C :   -0.277444    0.000038
 10 H :    0.132122    0.000055
 11 H :    0.132595    0.000027
 12 C :   -0.269954    0.002313
 13 H :    0.133533   -0.000056
 14 H :    0.133746    0.000202
 15 C :   -0.313993    0.008298
 16 H :    0.130675    0.001454
 17 H :    0.130268    0.002585
```

18 N :   -0.013259   0.077804
19 H :   0.180263   0.030881
20 H :   0.119552   0.021977
21 H :   0.136441   -0.000508
22 H :   0.149886   0.000217
23 H :   0.126791   0.000006
24 H :   0.126775   0.000001
25 N :   -0.202221   0.000050
26 H :   0.152414   0.000001
27 H :   0.152576   0.000001

Spermine

Radical 1

LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
----

0 H :   0.123136   0.001687
1 H :   0.135691   0.005826
2 C :   -0.315684   0.617804
3 C :   -0.337545   0.035670
4 C :   -0.305326   0.056777
5 N :   -0.199117   0.004589
6 H :   0.124271   0.006120
7 H :   0.141960   0.004565
8 C :   -0.314513   0.000348
9 C :   -0.272402   0.003265
10 H :   0.129945   0.001458
11 H :   0.133335   0.000095
12 C :   -0.263587   0.000046
13 H :   0.139443   0.000090
14 H :   0.137434   -0.000093
15 C :   -0.289354   0.019742
16 H :   0.134889   0.001932
17 H :   0.120187   0.012903
18 N :   0.058333   0.211374
19 H :   0.185290   0.007255
20 H :   0.119140   0.007599
21 H :   0.142806   0.000704
22 H :   0.152595   0.000058
23 H :   0.128928   0.000121
24 H :   0.130313   0.000022
25 N :   -0.023386   0.000001
26 H :   0.149129   -0.000000
27 H :   0.139974   0.000001
28 H :   0.125860   -0.000000
29 N :   -0.212562   -0.000000
30 C :   -0.340731   0.000000

31 C :   -0.279738   0.000002
32 C :   -0.309956   0.000036
33 H :   0.134992   -0.000002
34 H :   0.132812   0.000000
35 H :   0.125665   0.000000
36 H :   0.170604   0.000001
37 H :   0.116485   0.000002
38 H :   0.130683   0.000001

Radical 2

LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
----
0 H :   0.127187   0.000002
1 H :   0.134595   -0.000082
2 C :   -0.291974   0.019351
3 C :   -0.338905   0.000917
4 C :   -0.277362   -0.000047
5 N :   -0.205578   0.005165
6 H :   0.127239   0.000010
7 H :   0.141940   0.000067
8 C :   -0.316320   0.003938
9 C :   -0.268562   0.033713
10 H :   0.129806   -0.000232
11 H :   0.130417   0.000768
12 C :   -0.289152   0.055391
13 H :   0.140681   0.002638
14 H :   0.138499   0.007496
15 C :   -0.310820   0.628325
16 H :   0.118978   0.008213
17 N :   0.058047   0.201727
18 H :   0.186142   0.007326
19 H :   0.120493   0.013019
20 H :   0.139367   0.004518
21 H :   0.151133   0.000492
22 H :   0.129025   0.000054
23 H :   0.130034   0.000019
24 N :   -0.023621   0.004069
25 H :   0.135500   0.001921
26 H :   0.149226   0.000016
27 H :   0.139938   0.000027
28 H :   0.125870   0.000002
29 N :   -0.212613   0.000148
30 C :   -0.340928   0.000030
31 C :   -0.279782   0.000036
32 C :   -0.309793   0.000400

33	H :	0.134952	0.000162
34	H :	0.132828	0.000001
35	H :	0.125598	0.000003
36	H :	0.170549	0.000084
37	H :	0.116672	0.000300
38	H :	0.130692	0.000012

Radical 3

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LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS

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0	H :	0.125861	0.000001
1	H :	0.132850	-0.000000
2	C :	-0.310841	0.000031
3	C :	-0.340566	0.000018
4	C :	-0.279224	0.000009
5	N :	-0.210897	0.000078
6	H :	0.125998	0.000003
7	H :	0.140180	0.000003
8	C :	-0.303323	0.015248
9	C :	-0.271143	0.012310
10	H :	0.130374	0.002607
11	H :	0.134073	-0.000117
12	C :	-0.264229	0.000694
13	H :	0.138330	0.000467
14	H :	0.136307	0.000009
15	C :	-0.308103	0.000642
16	H :	0.130128	-0.000001
17	H :	0.115813	0.000081
18	N :	-0.023216	0.000155
19	H :	0.173340	0.000011
20	H :	0.115310	0.000005
21	H :	0.136608	-0.000014
22	H :	0.149469	0.000007
23	H :	0.131445	0.000460
24	H :	0.132891	0.000720
25	N :	0.026261	0.183659
26	H :	0.130057	0.000002
27	H :	0.151485	0.000099
28	H :	0.140572	0.002312
29	H :	0.128062	0.005161
30	N :	-0.204425	0.009032
31	C :	-0.337178	0.029507

32 C :   -0.306084   0.051707
33 C :   -0.268895   0.658918
34 H :   0.139972   0.003770
35 H :   0.133436   0.002515
36 H :   0.126300   0.000292
37 H :   0.181219   0.006377
38 H :   0.121782   0.013220

Radical 4

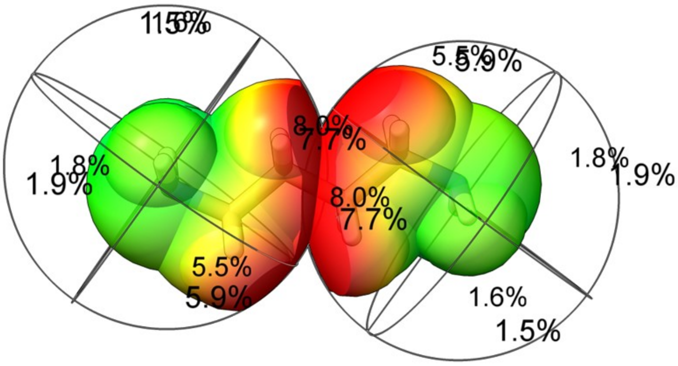
LOEWDIN ATOMIC CHARGES AND SPIN POPULATIONS
----

0 H :   0.125906   -0.000001
1 H :   0.132901   -0.000000
2 C :   -0.310613   0.000473
3 C :   -0.340436   0.000013
4 C :   -0.279181   -0.000003
5 N :   -0.210961   0.000054
6 H :   0.126047   0.000004
7 H :   0.140250   0.000008
8 C :   -0.219631   0.751535
9 C :   -0.283559   0.066647
10 H :   0.139382   0.030152
11 H :   0.136599   0.005097
12 C :   -0.266800   0.003524
13 H :   0.137760   0.001478
14 H :   0.135994   -0.000123
15 C :   -0.309040   -0.000507
16 H :   0.130086   0.000026
17 H :   0.115738   -0.000147
18 N :   -0.022951   0.003251
19 H :   0.173526   0.000090
20 H :   0.115545   0.000147
21 H :   0.136482   0.000200
22 H :   0.149575   -0.000003
23 H :   0.119819   0.005864
24 N :   -0.015499   0.085535
25 H :   0.130145   0.000015
26 H :   0.150065   0.000110
27 H :   0.141762   0.001011
28 H :   0.126657   -0.000033
29 N :   -0.210169   0.001750
30 C :   -0.339832   0.000471
31 C :   -0.278289   0.003085

32 C :	-0.303167	0.036313
33 H :	0.136989	0.000693
34 H :	0.133987	-0.000087
35 H :	0.126290	0.000034
36 H :	0.173892	0.001019
37 H :	0.121069	0.001286
38 H :	0.133663	0.001019

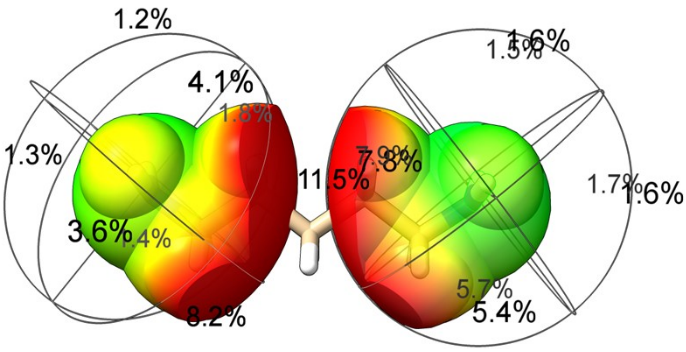
Table S7: Buried volume at main amine radical site

Putrascine



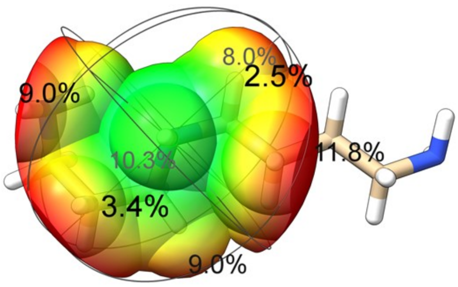
% Buried volume at radical centre = 33.8

Cadavarine



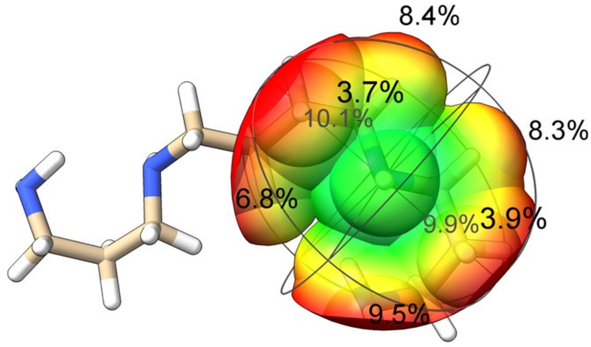
% Buried volume at radical centre = 33.2

Spermidine



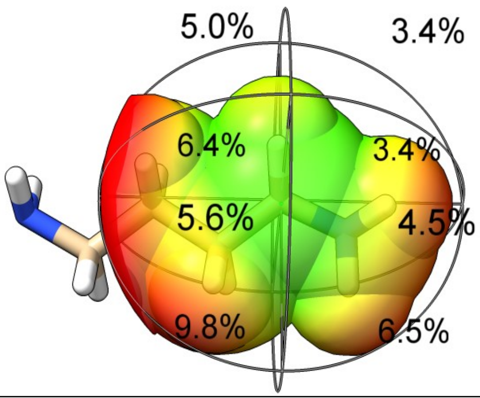
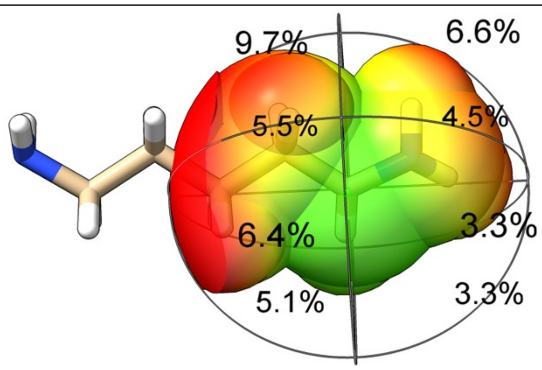
% Buried volume at radical centre = 56.5

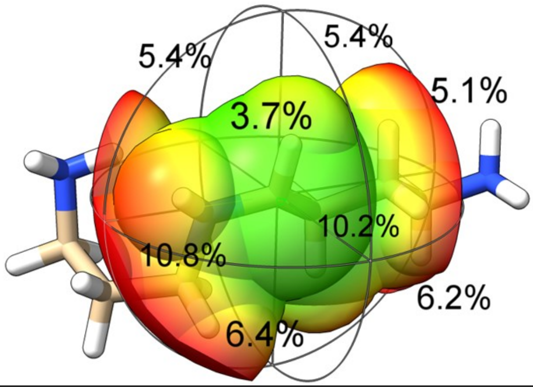
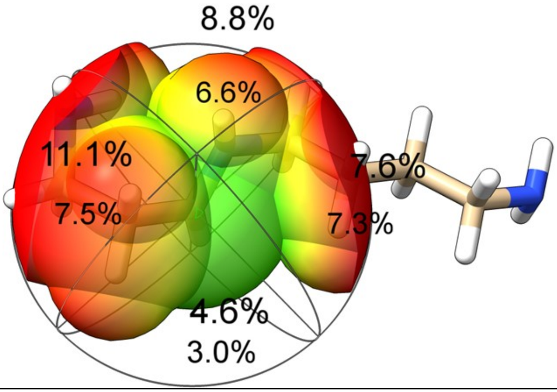
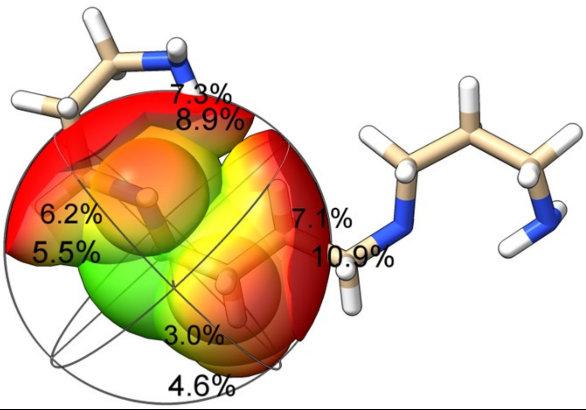
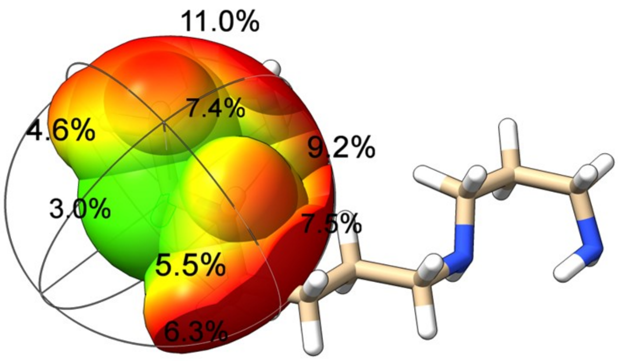
Spermine

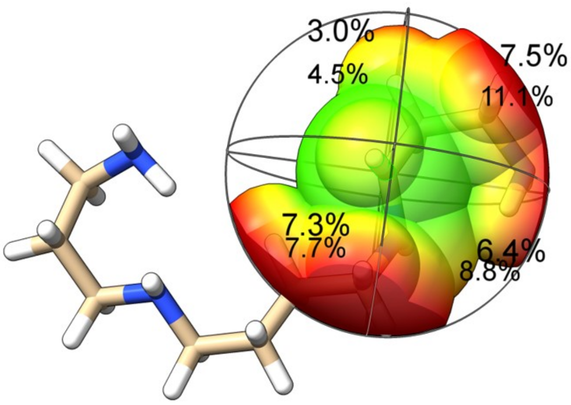
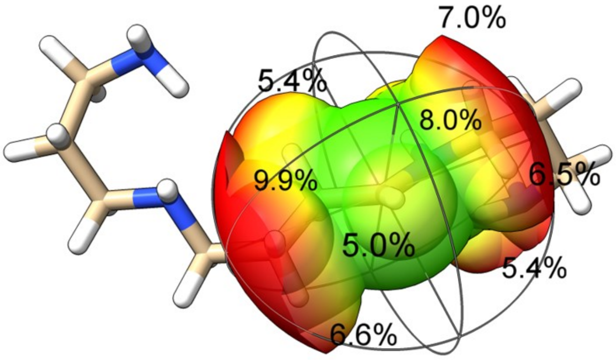


% Buried volume at radical centre = 60.7

Images generated with chimera and buried volume calculated using SEQCROW.

Table S8: Buried volume at carbon radical site	**% Buried volume at radical centre (% V_{bur})**
Putrascine	
	**44.6**
Cadavarine	
	**44.4**

<table>
<tr><td colspan="2">Spermidine</td></tr>
<tr><td>Radical 1

</td><td>53.1</td></tr>
<tr><td>Radical 2

</td><td>56.5</td></tr>
<tr><td colspan="2">Spermine</td></tr>
<tr><td>Radical 1

</td><td>53.6</td></tr>
<tr><td>Radical 2

</td><td>54.5</td></tr>
</table>

Radical 3 	56.3
Radical 4 	53.8

Images generated with chimera and buried volume calculated using SEQCROW [5].

Table S9. Comparison of the developed system with other ECL methodologies for spermine detection

S. no.	Analytical method	Linear range	LOD	Ref.
1.	ECL-CE	0.25 μM – 0.5 μM	0.2 μM	[6]
2.	Electrochemical analysis	3 μM to 300 μM	1 μM	[7]
3.	Luminescence analysis	5 μM to 0.5 mM	0.5 μM	[8]
4.	Solid-state ECL method	10 nM to 100 nM	12.2 nM	This work

Table S10. Quantification and recovery studies of spermine content in urine sample using developed ECL detection method.

Sample No.	Original content (10^{-9} M)	Added (10^{-9} M)	Found (10^{-9} M)	Recovery (%)	*t*-test
1.	13.2	10 nM	13.3±0.004	105 %	0.495
2.		30 nM	20.6±0.001	93.5 %	0.012
3.		50 nM	49.6±0.12	86.4 %	0.866

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