Electronic Supplementary Material (ESI) for RSC Advances.

Theoretical-computational modeling of charge transfer and intersystem crossing re actions in complex chemical systems

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Supplementary Information

Contents:

S1. Gromacs-format Topology of DMN in the S3 electronic state utilized in the NonEqMD (sse text)

```
[ moleculetype ]
; Name nrexcl
 dmn     3
   1_2    NBB    1   2.065   2.317   2.871
    1_2    CAY    2   2.142   2.290   2.792
    1_2    CAV    3   2.235   2.266   2.685
    1_2    CAX    4   2.321   2.379   2.666
    1_2    NBC    5   2.401   2.459   2.682
    1_2    CAT    6   2.213   2.179   2.588
    1_2    CAB    7   2.091   2.161   2.524
    1_2    CAA    8   2.071   2.014   2.559
    1_2    CAF    9   2.212   1.958   2.547
    1_2    CAE   10   2.290   2.086   2.519
    1_2    CAD   11   2.279   2.147   2.381
    1_2    CAC   12   2.140   2.207   2.388
    1_2    CAJ   13   2.083   2.189   2.248
    1_2    CAS   14   2.132   2.051   2.208
    1_2    CAG   15   2.276   2.085   2.242
    1_2    CAH   16   2.282   2.197   2.159
    1_2    CAI   17   2.166   2.262   2.163
    1_2    CAK   18   2.128   2.352   2.072
```

```
    1_2    OAU   19   2.059   2.451   2.134
    1_2    CAZ   20   1.926   2.472   2.088
    1_2    CAL   21   2.220   2.385   1.973
    1_2    CAO   22   2.166   2.453   1.865
    1_2    HAO   23   2.072   2.507   1.873
    1_2    CAP   24   2.240   2.450   1.748
    1_2    HAP   25   2.233   2.535   1.679
    1_2    CAQ   26   2.359   2.380   1.732
    1_2    HAQ   27   2.379   2.325   1.640
    1_2    CAR   28   2.410   2.326   1.850
    1_2    HAR   29   2.504   2.272   1.836
    1_2    CAM   30   2.345   2.323   1.972
    1_2    CAN   31   2.374   2.228   2.069
    1_2    OAW   32   2.499   2.202   2.117
    1_2    CBA   33   2.629   2.199   2.059
[ atoms ]
;   nr       type  resnr resid  atom  cgnr    charge      mass
     1         N     1   _2     NBB     1 -0.506302    14.0067
     2         C     1   _2     CAY     1  0.491696    12.0110
     3         C     1   _2     CAV     1 -0.398920    12.0110
     4         C     1   _2     CAX     2  0.495441    12.0110
     5         N     1   _2     NBC     2 -0.508099    14.0067
     6         C     1   _2     CAT     2  0.293006    12.0110
     7       CH2     1   _2     CAB     2 -0.064972    13.0190
     8       CH1     1   _2     CAA     2  0.020227    14.0270
     9       CH1     1   _2     CAF     2  0.032816    14.0270
    10       CH2     1   _2     CAE     2 -0.102442    13.0190
    11       CH1     1   _2     CAD     3  0.044276    13.0190
    12       CH1     1   _2     CAC     3 -0.004646    13.0190
    13       CH2     1   _2     CAJ     3  0.280741    13.0190
    14       CH1     1   _2     CAS     4 -0.148762    14.0270
    15       CH2     1   _2     CAG     4  0.229046    13.0190
    16         C     1   _2     CAH     4 -0.061371    12.0110
    17         C     1   _2     CAI     4 -0.200545    12.0110
    18         C     1   _2     CAK     4  0.195138    12.0110
    19        OA     1   _2     OAU     4 -0.355760    15.9994
    20       CH3     1   _2     CAZ     4  0.262069    15.0350
    21         C     1   _2     CAL     5  0.029026    12.0110
    22       CR1     1   _2     CAO     5 -0.107860    12.0110
    23        HC     1   _2     HAO     5  0.084225     1.0080
    24       CR1     1   _2     CAP     5 -0.109683    12.0110
    25        HC     1   _2     HAP     5  0.075817     1.0080
    26       CR1     1   _2     CAQ     6 -0.092679    12.0110
    27        HC     1   _2     HAQ     6  0.076830     1.0080
    28       CR1     1   _2     CAR     6 -0.117333    12.0110
    29        HC     1   _2     HAR     6  0.083461     1.0080
    30         C     1   _2     CAM     6  0.017430    12.0110
    31         C     1   _2     CAN     6  0.102043    12.0110
    32        OA     1   _2     OAW     6 -0.272116    15.9994
    33       CH3     1   _2     CBA     6  0.238203    15.0350

[ bonds ]
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; ai  aj  fu    c0, c1, ...
   2   1   2    0.114   4560970.4
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   3   4   2    0.143   3724162.7
   6   3   2    0.133  11800000.0
   4   5   2    0.114   4560970.4
   7   6   2    0.139   8660000.0
  10   6   2    0.139   8660000.0
   7   8   2    0.152   5430000.0
   7  12   2    0.152   5430000.0
   8   9   2    0.152   5430000.0
  10   9   2    0.152   5430000.0
  10  11   2    0.152   5430000.0
  11  12   2    0.152   5430000.0
  11  15   2    0.152   5430000.0
  12  13   2    0.152   5430000.0
  13  14   2    0.152   5430000.0
  13  17   2    0.139   8660000.0
  15  14   2    0.152   5430000.0
  15  16   2    0.139   8660000.0
  16  17   2    0.133  11800000.0
  16  31   2    0.133  11800000.0
  17  18   2    0.133  11800000.0
  18  19   2    0.136  10200000.0
  18  21   2    0.139  10800000.0
  19  20   2    0.143   8180000.0
  21  22   2    0.139  10800000.0
  21  30   2    0.139  10800000.0
  22  23   2    0.109  12300000.0
  22  24   2    0.139  10800000.0
  24  25   2    0.109  12300000.0
  24  26   2    0.139  10800000.0
  26  27   2    0.109  12300000.0
  26  28   2    0.139  10800000.0
  28  29   2    0.109  12300000.0
  30  28   2    0.139  10800000.0
  30  31   2    0.139  10800000.0
  31  32   2    0.136  10200000.0
  32  33   2    0.143   8180000.0

[ pairs ]
; ai  aj  fu    c0, c1, ...
   1   4   1                          ;  NBB  CAX
   1   6   1                          ;  NBB  CAT
   2   5   1                          ;  CAY  NBC
   2   7   1                          ;  CAY  CAB
   2  10   1                          ;  CAY  CAE
   3   8   1                          ;  CAV  CAA
   3   9   1                          ;  CAV  CAF
   3  11   1                          ;  CAV  CAD
   3  12   1                          ;  CAV  CAC
   4   7   1                          ;  CAX  CAB
```

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 4 10  1                    ;  CAX  CAE
 5  6  1                    ;  NBC  CAT
 6 13  1                    ;  CAT  CAJ
 6 15  1                    ;  CAT  CAG
 7 14  1                    ;  CAB  CAS
 7 15  1                    ;  CAB  CAG
 7 17  1                    ;  CAB  CAI
 8 11  1                    ;  CAA  CAD
 8 13  1                    ;  CAA  CAJ
 9 12  1                    ;  CAF  CAC
 9 15  1                    ;  CAF  CAG
10 13  1                    ;  CAE  CAJ
10 14  1                    ;  CAE  CAS
10 16  1                    ;  CAE  CAH
11 17  1                    ;  CAD  CAI
11 31  1                    ;  CAD  CAN
12 16  1                    ;  CAC  CAH
12 18  1                    ;  CAC  CAK
13 19  1                    ;  CAJ  OAU
13 21  1                    ;  CAJ  CAL
13 31  1                    ;  CAJ  CAN
14 18  1                    ;  CAS  CAK
14 31  1                    ;  CAS  CAN
15 18  1                    ;  CAG  CAK
15 30  1                    ;  CAG  CAM
15 32  1                    ;  CAG  OAW
16 19  1                    ;  CAH  OAU
16 21  1                    ;  CAH  CAL
16 28  1                    ;  CAH  CAR
16 33  1                    ;  CAH  CBA
17 20  1                    ;  CAI  CAZ
17 22  1                    ;  CAI  CAO
17 30  1                    ;  CAI  CAM
17 32  1                    ;  CAI  OAW
18 23  1                    ;  CAK  HAO
18 24  1                    ;  CAK  CAP
18 28  1                    ;  CAK  CAR
18 31  1                    ;  CAK  CAN
19 22  1                    ;  OAU  CAO
19 30  1                    ;  OAU  CAM
20 21  1                    ;  CAZ  CAL
21 25  1                    ;  CAL  HAP
21 26  1                    ;  CAL  CAQ
21 29  1                    ;  CAL  HAR
21 32  1                    ;  CAL  OAW
22 27  1                    ;  CAO  HAQ
22 28  1                    ;  CAO  CAR
22 31  1                    ;  CAO  CAN
23 25  1                    ;  HAO  HAP
23 26  1                    ;  HAO  CAQ
23 30  1                    ;  HAO  CAM
24 29  1                    ;  CAP  HAR
```

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  24  30   1                          ;  CAP  CAM
  25  27   1                          ;  HAP  HAQ
  25  28   1                          ;  HAP  CAR
  26  31   1                          ;  CAQ  CAN
  27  29   1                          ;  HAQ  HAR
  27  30   1                          ;  HAQ  CAM
  28  32   1                          ;  CAR  OAW
  29  31   1                          ;  HAR  CAN
  30  33   1                          ;  CAM  CBA

[ angles ]
; ai  aj  ak  fu    c0, c1, ...
   1   2   3   2    180.0      4000.4
   2   3   4   2    115.0       610.0
   2   3   6   2    115.0       610.0
   4   3   6   2    115.0       610.0
   3   4   5   2    180.0      4000.4
   3   6   7   2    120.0       560.0
   3   6  10   2    120.0       560.0
   7   6  10   2    108.0       465.0
   6   7   8   2    104.0       444.4
   6   7  12   2    104.0       444.4
   8   7  12   2    109.5       520.0
   7   8   9   2    104.0       444.4
   8   9  10   2    104.0       444.4
   6  10   9   2    104.0       444.4
   6  10  11   2    104.0       444.4
   9  10  11   2    109.5       520.0
  10  11  12   2    104.0       444.4
  10  11  15   2    109.5       520.0
  12  11  15   2    104.0       444.4
   7  12  11   2    104.0       444.4
   7  12  13   2    109.5       520.0
  11  12  13   2    104.0       444.4
  12  13  14   2    104.0       444.4
  12  13  17   2    109.5       520.0
  14  13  17   2    104.0       444.4
  13  14  15   2    104.0       444.4
  11  15  14   2    104.0       444.4
  11  15  16   2    109.5       520.0
  14  15  16   2    104.0       444.4
  15  16  17   2    108.0       465.0
  15  16  31   2    132.0       760.0
  17  16  31   2    120.0       560.0
  13  17  16   2    108.0       465.0
  13  17  18   2    132.0       760.0
  16  17  18   2    120.0       560.0
  17  18  19   2    115.0       610.0
  17  18  21   2    120.0       560.0
  19  18  21   2    115.0       610.0
  18  19  20   2    109.5       380.0
  18  21  22   2    120.0       560.0
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  18  21  30   2    120.0      560.0
  22  21  30   2    120.0      560.0
  21  22  23   2    120.0      505.0
  21  22  24   2    120.0      505.0
  23  22  24   2    120.0      505.0
  22  24  25   2    120.0      505.0
  22  24  26   2    120.0      505.0
  25  24  26   2    120.0      505.0
  24  26  27   2    120.0      505.0
  24  26  28   2    120.0      505.0
  27  26  28   2    120.0      505.0
  26  28  29   2    120.0      505.0
  26  28  30   2    120.0      505.0
  29  28  30   2    120.0      505.0
  21  30  28   2    120.0      560.0
  21  30  31   2    120.0      560.0
  28  30  31   2    120.0      560.0
  16  31  30   2    120.0      560.0
  16  31  32   2    115.0      610.0
  30  31  32   2    115.0      610.0
  31  32  33   2    109.5      380.0

[ dihedrals ]
; ai  aj  ak  al  fu    c0, c1, m, ...
   3   6   4   2   2     0.0  167.4
   6  10   7   3   2     0.0  167.4
   7   6   8  12   2    35.3  334.8
  10  11   9   6   2    35.3  334.8
  11  10  12  15   2    35.3  334.8
  12  13  11   7   2    35.3  334.8
  13  12  14  17   2    35.3  334.8
  15  16  14  11   2    35.3  334.8
  16  15  31  17   2     0.0  167.4
  17  13  18  16   2     0.0  167.4
  18  17  19  21   2     0.0  167.4
  21  30  22  18   2     0.0  167.4
  22  21  24  23   2     0.0  167.4
  24  22  26  25   2     0.0  167.4
  26  24  28  27   2     0.0  167.4
  28  26  30  29   2     0.0  167.4
  30  31  28  21   2     0.0  167.4
  31  16  32  30   2     0.0  167.4
  21  22  24  26   2     0.0  209.3
  22  24  26  28   2     0.0  209.3
  24  26  28  30   2     0.0  209.3
  26  28  30  21   2     0.0  209.3
  28  30  21  22   2     0.0  209.3
  30  21  22  24   2     0.0  209.3
  16  17  18  21   2     0.0  209.3
  17  18  21  30   2     0.0  209.3
  18  21  30  31   2     0.0  209.3
  21  30  31  16   2     0.0  209.3
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 30  31  16  17   2      0.0  209.3
 31  16  17  18   2      0.0  209.3
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 12   7   6   3   1      0.0    1.0 6
 11  10   6   3   1      0.0    1.0 6
  9   8   7   6   1      0.0    5.9 3
 13  12   7   6   1      0.0    5.9 3
 10   9   8   7   1      0.0    5.9 3
 11  10   9   8   1      0.0    5.9 3
 15  11  10   6   1      0.0    5.9 3
 13  12  11  10   1      0.0    5.9 3
 16  15  11  10   1      0.0    5.9 3
 17  13  12   7   1      0.0    5.9 3
 15  14  13  12   1      0.0    5.9 3
 12  13  17  18   1      0.0    1.0 6
 16  15  14  13   1      0.0    5.9 3
 11  15  16  31   1      0.0    1.0 6
 17  18  19  20   1    180.0   16.7 2
 16  31  32  33   1    180.0   16.7 2
```

S2. DMN coordinates (gromos-format)

```
  1_2    NBB    1   2.065   2.317   2.871
  1_2    CAY    2   2.142   2.290   2.792
  1_2    CAV    3   2.235   2.266   2.685
  1_2    CAX    4   2.321   2.379   2.666
  1_2    NBC    5   2.401   2.459   2.682
  1_2    CAT    6   2.213   2.179   2.588
  1_2    CAB    7   2.091   2.161   2.524
  1_2    CAA    8   2.071   2.014   2.559
  1_2    CAF    9   2.212   1.958   2.547
  1_2    CAE   10   2.290   2.086   2.519
  1_2    CAD   11   2.279   2.147   2.381
  1_2    CAC   12   2.140   2.207   2.388
  1_2    CAJ   13   2.083   2.189   2.248
  1_2    CAS   14   2.132   2.051   2.208
  1_2    CAG   15   2.276   2.085   2.242
  1_2    CAH   16   2.282   2.197   2.159
  1_2    CAI   17   2.166   2.262   2.163
  1_2    CAK   18   2.128   2.352   2.072
  1_2    OAU   19   2.059   2.451   2.134
  1_2    CAZ   20   1.926   2.472   2.088
  1_2    CAL   21   2.220   2.385   1.973
  1_2    CAO   22   2.166   2.453   1.865
  1_2    HAO   23   2.072   2.507   1.873
  1_2    CAP   24   2.240   2.450   1.748
  1_2    HAP   25   2.233   2.535   1.679
  1_2    CAQ   26   2.359   2.380   1.732
  1_2    HAQ   27   2.379   2.325   1.640
  1_2    CAR   28   2.410   2.326   1.850
  1_2    HAR   29   2.504   2.272   1.836
  1_2    CAM   30   2.345   2.323   1.972
```

1_2	CAN	31	2.374	2.228	2.069
1_2	OAW	32	2.499	2.202	2.117
1_2	CBA	33	2.629	2.199	2.059

S3. DMN geometries Optimized at the B3LYP/6-311G level**

S0

c	3.35352	-0.0597	0.19227
c	2.76038	-1.01972	-0.81536
c	3.32233	-0.38833	-2.11889
c	3.34282	1.14945	-1.80375
c	2.78691	1.23197	-0.35499
c	1.27143	0.85954	-0.22927
c	1.25325	-0.69198	-0.54675
c	0.17685	1.42813	-1.19313
c	-1.15137	0.9074	-0.62023
c	-1.1481	-0.50277	-0.91202
c	0.14725	-0.80911	-1.6474
c	0.27634	0.51349	-2.44176
c	-2.16602	-1.33546	-0.53712
c	-3.29984	-0.78442	0.14431
c	-3.3116	0.61093	0.46706
c	-2.20323	1.45577	0.08506
c	-4.43806	1.14196	1.14808
c	-5.50782	0.33712	1.4884
c	-5.50243	-1.03493	1.15266
c	-4.42092	-1.58171	0.49187
c	-1.6029	-3.54547	0.12708
c	-1.49414	3.78587	0.04015
c	4.13064	-0.28875	1.27734
c	4.54368	-1.61856	1.63305
c	4.57266	0.78898	2.11917
h	-4.41701	-2.62931	0.21166
h	-6.35332	-1.65928	1.40968
h	-6.36006	0.76359	2.00938
h	-4.44569	2.19668	1.39454
h	0.143	-1.7421	-2.21299
h	0.24953	2.49652	-1.3818
h	1.19472	0.62241	-3.01098
h	-0.56962	0.66195	-3.11904
h	0.95102	-1.27368	0.32852
h	0.97734	1.05962	0.80507
h	3.06227	2.14365	0.1776
h	4.36718	1.53382	-1.81994
h	2.76536	1.75347	-2.50674
h	2.72958	-0.65364	-2.9966
h	4.33626	-0.76065	-2.29382
h	3.01182	-2.07339	-0.68515
h	-1.73647	-4.56485	-0.24082
h	-0.53306	-3.34982	0.27289
h	-2.1223	-3.43004	1.08616

h	-1.89503	4.70796	0.46449
h	-0.46725	3.64761	0.3965
h	-1.50445	3.85796	-1.05357
o	-2.15467	-2.67935	-0.87102
o	-2.35417	2.75282	0.49781
n	4.86908	-2.70147	1.90728
n	4.92196	1.67371	2.78927

S1 (TD-B3LYP/6-311G**)

c	-3.586008	-0.000021	-0.191959
c	-2.960704	-1.136753	0.628777
c	-3.483617	-0.785600	2.046449
c	-3.483496	0.786855	2.046052
c	-2.960712	1.137206	0.628110
c	-1.443263	0.792136	0.438154
c	-1.443197	-0.791657	0.438720
c	-0.326328	1.141714	1.478728
c	0.987798	0.702503	0.809890
c	0.987701	-0.701480	0.810324
c	-0.326199	-1.140331	1.479595
c	-0.425887	0.001081	2.530528
c	2.057477	-1.420169	0.251873
c	3.227086	-0.711628	-0.214525
c	3.227236	0.710784	-0.215213
c	2.057749	1.420291	0.250653
c	4.354853	1.397450	-0.697707
c	5.465084	0.698313	-1.156755
c	5.464917	-0.700648	-1.156110
c	4.354516	-1.399050	-0.696448
c	1.001284	-3.687049	0.221857
c	1.003571	3.688141	0.221885
c	-3.653768	-0.000357	-1.619537
c	-3.680434	-1.211790	-2.334992
c	-3.679677	1.210697	-2.335636
h	4.340895	-2.479079	-0.703694
h	6.328057	-1.243509	-1.518837
h	6.328341	1.240648	-1.519985
h	4.341671	2.477468	-0.705950
h	-0.345861	-2.149047	1.881660
h	-0.346346	2.150642	1.880169
h	-1.350806	0.001250	3.090771
h	0.417686	0.001457	3.227682
h	-1.158422	-1.177563	-0.545417
h	-1.158477	1.177413	-0.546212
h	-3.203945	2.151357	0.307873
h	-4.504755	1.163612	2.146721
h	-2.896921	1.230625	2.856571
h	-2.897222	-1.229066	2.857273
h	-4.504951	-1.162146	2.147139
h	-3.203821	-2.151120	0.309110
h	1.321703	-4.565296	-0.331943

h	0.833982	-3.940513	1.267545
h	0.110189	-3.255835	-0.229087
h	1.325606	4.567911	-0.328480
h	0.111882	3.259942	-0.230948
h	0.836091	3.937990	1.268348
o	2.138555	-2.758468	0.114731
o	2.139336	2.758306	0.111313
n	-3.669566	-2.256989	-2.882615
n	-3.668090	2.255608	-2.883804

S2 (TD-B3LYP/6-311G**)

c	-3.191387	-0.042664	-0.596440
c	-2.612460	-1.131156	0.326589
c	-3.209790	-0.709290	1.707275
c	-3.219693	0.859918	1.625759
c	-2.627801	1.143615	0.208086
c	-1.115470	0.801406	0.103388
c	-1.104323	-0.782077	0.186285
c	-0.066174	1.225038	1.194153
c	1.271766	0.799531	0.615463
c	1.272163	-0.683315	0.700539
c	-0.048847	-1.072755	1.315696
c	-0.205725	0.129206	2.294594
c	2.339082	-1.432123	0.285416
c	3.492535	-0.756726	-0.205838
c	3.497366	0.710647	-0.308712
c	2.352633	1.469391	0.090108
c	4.655668	1.355299	-0.812048
c	5.752589	0.623571	-1.186632
c	5.750959	-0.812762	-1.074198
c	4.649385	-1.474659	-0.596527
c	1.465230	-3.615613	-0.407297
c	1.360817	3.738644	-0.116747
c	-4.541673	-0.075250	-1.072536
c	-5.198647	-1.302292	-1.276472
c	-5.215057	1.117199	-1.393960
h	4.632919	-2.549281	-0.496824
h	6.632606	-1.364327	-1.372517
h	6.633812	1.119514	-1.570950
h	4.644504	2.431403	-0.886529
h	-0.076601	-2.068956	1.752090
h	-0.135438	2.252820	1.535926
h	-1.156875	0.151199	2.805679
h	0.599593	0.173725	3.034228
h	-0.759292	-1.213843	-0.757992
h	-0.775897	1.136796	-0.881682
h	-2.872073	2.138381	-0.166816
h	-4.246328	1.233879	1.644470
h	-2.689835	1.353426	2.447667
h	-2.676390	-1.109456	2.575786
h	-4.232099	-1.091605	1.763227

h	-2.843128	-2.162857	0.057932
h	1.705808	-4.648474	-0.168489
h	0.433219	-3.397813	-0.133244
h	1.617814	-3.426000	-1.472899
h	1.731159	4.621150	-0.633432
h	0.529423	3.301443	-0.671314
h	1.050241	4.006509	0.893321
o	2.409599	-2.813369	0.393749
o	2.503291	2.824719	-0.076502
n	-5.704332	-2.357718	-1.424640
n	-5.734114	2.146985	-1.642685

S3 (TD-B3LYP/6-311G**)

c	3.344480	0.125616	-0.233953
c	2.749358	1.047273	0.819883
c	3.362107	0.400044	2.097160
c	3.415305	-1.133067	1.744338
c	2.820878	-1.197440	0.305900
c	1.288734	-0.867234	0.247811
c	1.239450	0.682907	0.603354
c	0.244174	-1.488334	1.245779
c	-1.110731	-0.962375	0.732678
c	-1.130240	0.395647	1.052718
c	0.173212	0.742603	1.755161
c	0.374827	-0.597758	2.515689
c	-2.139286	1.255055	0.569669
c	-3.288606	0.738014	-0.113626
c	-3.257380	-0.638418	-0.499375
c	-2.145886	-1.467326	-0.091701
c	-4.338909	-1.184940	-1.240490
c	-5.459271	-0.368269	-1.553668
c	-5.523144	0.940636	-1.130114
c	-4.446636	1.517295	-0.395082
c	-2.298573	3.666821	-0.078721
c	-1.347858	-3.824286	-0.140547
c	4.097875	0.395953	-1.322699
c	4.473989	1.735592	-1.650103
c	4.546006	-0.648576	-2.189706
h	-4.561848	2.500313	0.035131
h	-6.393686	1.548007	-1.351449
h	-6.274979	-0.796256	-2.126097
h	-4.307750	-2.217696	-1.546331
h	0.162375	1.662008	2.335657
h	0.342256	-2.558011	1.405930
h	1.318379	-0.693434	3.039260
h	-0.440343	-0.784549	3.218588
h	0.880144	1.275224	-0.242168
h	0.955956	-1.049995	-0.777936
h	3.101137	-2.089776	-0.252507
h	4.450216	-1.486127	1.724218
h	2.872100	-1.766076	2.446811

h	2.782041	0.626181	2.992285
h	4.370610	0.792034	2.256048
h	2.964941	2.109071	0.710296
h	-3.043257	4.282103	0.425986
h	-1.392246	4.247082	-0.252359
h	-2.703683	3.272151	-1.007841
h	-1.745624	-4.711489	-0.627553
h	-0.331234	-3.633653	-0.491596
h	-1.357022	-3.958065	0.943717
o	-1.904751	2.579247	0.830772
o	-2.245968	-2.753930	-0.538433
n	4.769548	2.838416	-1.900962
n	4.901027	-1.519013	-2.884600

S4. Gromacs-format topology of singlet FL

[atoms]

; nr	type	resnr	resid	atom	cgnr	charge	mass
1	CH2	1	_2	CAM	1	0.350	14.0270
2	C	1	_2	CAD	1	-0.350	12.0110
3	CR1	1	_2	CAC	1	-0.050	12.0110
4	HC	1	_2	HAC	1	0.100	1.0080
5	CR1	1	_2	CAB	1	-0.050	12.0110
6	HC	1	_2	HAB	1	0.100	1.0080
7	CR1	1	_2	CAA	1	-0.050	12.0110
8	HC	1	_2	HAA	1	0.100	1.0080
9	CR1	1	_2	CAF	1	-0.050	12.0110
10	HC	1	_2	HAF	1	0.100	1.0080
11	C	1	_2	CAE	1	-0.025	12.0110
12	C	1	_2	CAH	2	-0.025	12.0110
13	C	1	_2	CAG	2	-0.350	12.0110
14	CR1	1	_2	CAI	2	-0.050	12.0110
15	HC	1	_2	HAI	2	0.100	1.0080
16	CR1	1	_2	CAJ	2	-0.050	12.0110
17	HC	1	_2	HAJ	2	0.100	1.0080
18	CR1	1	_2	CAL	2	-0.050	12.0110
19	HC	1	_2	HAL	2	0.100	1.0080
20	CR1	1	_2	CAK	2	-0.050	12.0110
21	HC	1	_2	HAK	2	0.100	1.0080

[bonds]

; ai	aj	fu	c0, c1, ...
2	1	2	0.139 8660000.0
13	1	2	0.139 8660000.0
2	3	2	0.133 11800000.0
2	11	2	0.133 11800000.0
3	4	2	0.109 12300000.0
3	5	2	0.139 10800000.0
5	6	2	0.109 12300000.0

```
  5   7   2    0.139  10800000.0
  7   8   2    0.109  12300000.0
  7   9   2    0.139  10800000.0
  9  10   2    0.109  12300000.0
 11   9   2    0.133  11800000.0
 11  12   2    0.133  11800000.0
 12  13   2    0.133  11800000.0
 12  20   2    0.133  11800000.0
 13  14   2    0.133  11800000.0
 14  15   2    0.109  12300000.0
 14  16   2    0.139  10800000.0
 16  17   2    0.109  12300000.0
 16  18   2    0.139  10800000.0
 18  19   2    0.109  12300000.0
 18  20   2    0.139  10800000.0
 20  21   2    0.109  12300000.0


[ pairs ]
; ai  aj  fu    c0, c1, ...
   1   4   1
   1   5   1
   1   9   1
   1  15   1
   1  16   1
   1  20   1
   2   6   1
   2   7   1
   2  10   1
   2  14   1
   2  20   1
   3   8   1
   3   9   1
   3  12   1
   3  13   1
   4   6   1
   4   7   1
   4  11   1
   5  10   1
   5  11   1
   6   8   1
   6   9   1
   7  12   1
   8  10   1
   8  11   1
   9  13   1
   9  20   1
  10  12   1
  11  14   1
  11  18   1
  11  21   1
  12  15   1
```

```
  12  16   1
  12  19   1
  13  17   1
  13  18   1
  13  21   1
  14  19   1
  14  20   1
  15  17   1
  15  18   1
  16  21   1
  17  19   1
  17  20   1
  19  21   1

[ angles ]
; ai  aj  ak  fu    c0, c1, ...
   2   1  13   2    104.0       444.4
   1   2   3   2    132.0       760.0
   1   2  11   2    108.0       465.0
   3   2  11   2    120.0       560.0
   2   3   4   2    120.0       505.0
   2   3   5   2    120.0       505.0
   4   3   5   2    120.0       505.0
   3   5   6   2    120.0       505.0
   3   5   7   2    120.0       505.0
   6   5   7   2    120.0       505.0
   5   7   8   2    120.0       505.0
   5   7   9   2    120.0       505.0
   8   7   9   2    120.0       505.0
   7   9  10   2    120.0       505.0
   7   9  11   2    120.0       505.0
  10   9  11   2    120.0       505.0
   2  11   9   2    120.0       560.0
   2  11  12   2    108.0       465.0
   9  11  12   2    132.0       760.0
  11  12  13   2    108.0       465.0
  11  12  20   2    132.0       760.0
  13  12  20   2    120.0       560.0
   1  13  12   2    108.0       465.0
   1  13  14   2    132.0       760.0
  12  13  14   2    120.0       560.0
  13  14  15   2    120.0       505.0
  13  14  16   2    120.0       505.0
  15  14  16   2    120.0       505.0
  14  16  17   2    120.0       505.0
  14  16  18   2    120.0       505.0
  17  16  18   2    120.0       505.0
  16  18  19   2    120.0       505.0
  16  18  20   2    120.0       505.0
  19  18  20   2    120.0       505.0
  12  20  18   2    120.0       505.0
  12  20  21   2    120.0       505.0
```

```
 18  20  21   2    120.0       505.0

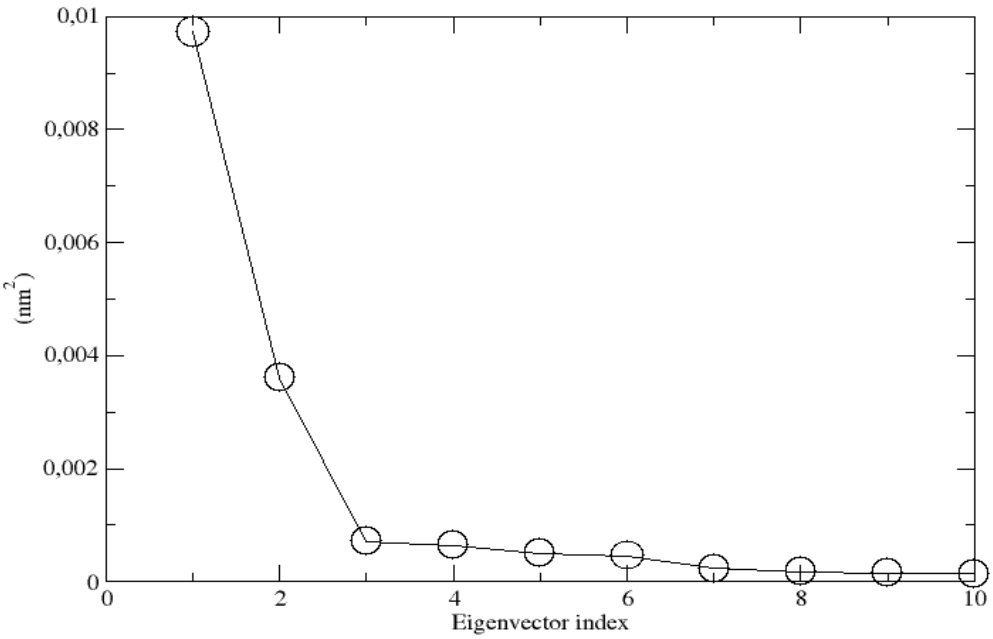

[ dihedrals ]
; ai  aj  ak  al  fu    c0, c1, m, ...
  2   1   3  11   2       0.0  167.4
  3   2   5   4   2       0.0  167.4
  5   3   7   6   2       0.0  167.4
  7   5   9   8   2       0.0  167.4
  9   7  11  10   2       0.0  167.4
 11  12   9   2   2       0.0  167.4
 12  20  13  11   2       0.0  167.4
 13   1  14  12   2       0.0  167.4
 14  13  16  15   2       0.0  167.4
 16  14  18  17   2       0.0  167.4
 18  16  20  19   2       0.0  167.4
 20  12  18  21   2       0.0  167.4
 12  13  14  16   2       0.0  209.3
 13  14  16  18   2       0.0  209.3
 14  16  18  20   2       0.0  209.3
 16  18  20  12   2       0.0  209.3
 18  20  12  13   2       0.0  209.3
 20  12  13  14   2       0.0  209.3
  2   3   5   7   2       0.0  209.3
  3   5   7   9   2       0.0  209.3
  5   7   9  11   2       0.0  209.3
  7   9  11   2   2       0.0  209.3
  9  11   2   3   2       0.0  209.3
 11   2   3   5   2       0.0  209.3
 13   1   2   3   1       0.0    2.1 6
  2   1  13  14   1       0.0    2.1 6
 20  12  11   2   1     180.0    4.9 2
```

S5. Gromos-format coordinates of singlet FL utilized in the MD simulation

```
  1_2    C     1   1.166   0.742   2.200
  1_2    C     2   1.263   0.821   2.260
  1_2    C     3   1.334   0.795   2.370
  1_2    H     4   1.337   0.694   2.409
  1_2    C     5   1.436   0.883   2.407
  1_2    H     6   1.506   0.864   2.488
  1_2    C     7   1.445   0.996   2.327
  1_2    H     8   1.537   1.055   2.330
  1_2    C     9   1.371   1.014   2.211
  1_2    H    10   1.376   1.111   2.161
  1_2    C    11   1.281   0.923   2.176
  1_2    C    12   1.203   0.914   2.069
  1_2    C    13   1.141   0.796   2.074
  1_2    C    14   1.070   0.754   1.970
  1_2    H    15   1.004   0.667   1.973
  1_2    C    16   1.052   0.838   1.861
```

1_2	H	17	0.967	0.819	1.796
1_2	C	18	1.116	0.961	1.855
1_2	H	19	1.153	0.996	1.758
1_2	C	20	1.196	0.994	1.963
1_2	H	21	1.251	1.088	1.958

S6. Spectrum of the eigenvalues as obtained from the diagonalization of the all-atom covariance matrix for singlet FL.



The two essential modes roughly correspond to the low-frequency out-of-plane normal modes of singlet carbene.

S7. Geometries extracted bt the essential plane and optimized in internal coordinates (by keeping frozen all the dihedral angles) at the B3LYP/6-311G level of theory**

REMARK GENERATED BY TRJCONV
TITLE bifenil in water t= 1.00000
REMARK THIS IS A SIMULATION BOX
CRYST1 25.748 22.865 22.968 90.00 90.00 90.00 P 1 1
MODEL 1
ATOM 1 C _2 1 1.139 -0.891 0.000 1.00 0.00
ATOM 2 C _2 1 0.001 -1.827 0.000 1.00 0.00
ATOM 3 C _2 1 -1.138 -0.893 -0.001 1.00 0.00
ATOM 4 C _2 1 -0.743 0.476 0.000 1.00 0.00
ATOM 5 C _2 1 0.742 0.477 0.000 1.00 0.00
ATOM 6 C _2 1 -2.487 -1.229 -0.001 1.00 0.00
ATOM 7 H _2 1 -2.774 -2.275 -0.001 1.00 0.00

```
ATOM      8  C   _2     1      -3.449  -0.205   0.000  1.00  0.00
ATOM      9  H   _2     1      -4.506  -0.449   0.001  1.00  0.00
ATOM     10  C   _2     1      -3.048   1.126   0.000  1.00  0.00
ATOM     11  H   _2     1      -3.800   1.909   0.001  1.00  0.00
ATOM     12  C   _2     1      -1.682   1.485   0.000  1.00  0.00
ATOM     13  H   _2     1      -1.400   2.534   0.001  1.00  0.00
ATOM     14  C   _2     1       1.680   1.488   0.000  1.00  0.00
ATOM     15  H   _2     1       1.397   2.536   0.000  1.00  0.00
ATOM     16  C   _2     1       3.046   1.130   0.000  1.00  0.00
ATOM     17  H   _2     1       3.797   1.915  -0.001  1.00  0.00
ATOM     18  C   _2     1       3.449  -0.201   0.000  1.00  0.00
ATOM     19  H   _2     1       4.507  -0.443   0.000  1.00  0.00
ATOM     20  C   _2     1       2.489  -1.225   0.000  1.00  0.00
ATOM     21  H   _2     1       2.777  -2.272   0.001  1.00  0.00
TER
ENDMDL
REMARK    GENERATED BY TRJCONV
TITLE     bifenil in water t=   2.00000
REMARK    THIS IS A SIMULATION BOX
CRYST1   25.748   22.865   22.968  90.00  90.00  90.00 P 1           1
MODEL        2
ATOM      1  C   _2     1       1.138  -0.893  -0.078  1.00  0.00
ATOM      2  C   _2     1       0.002  -1.826   0.009  1.00  0.00
ATOM      3  C   _2     1      -1.136  -0.893   0.067  1.00  0.00
ATOM      4  C   _2     1      -0.742   0.475   0.018  1.00  0.00
ATOM      5  C   _2     1       0.741   0.476  -0.030  1.00  0.00
ATOM      6  C   _2     1      -2.485  -1.227   0.001  1.00  0.00
ATOM      7  H   _2     1      -2.773  -2.274  -0.012  1.00  0.00
ATOM      8  C   _2     1      -3.446  -0.205  -0.022  1.00  0.00
ATOM      9  H   _2     1      -4.503  -0.450  -0.054  1.00  0.00
ATOM     10  C   _2     1      -3.046   1.127  -0.001  1.00  0.00
ATOM     11  H   _2     1      -3.797   1.910  -0.013  1.00  0.00
ATOM     12  C   _2     1      -1.680   1.485   0.012  1.00  0.00
ATOM     13  H   _2     1      -1.399   2.534  -0.009  1.00  0.00
ATOM     14  C   _2     1       1.678   1.486  -0.010  1.00  0.00
ATOM     15  H   _2     1       1.393   2.534   0.021  1.00  0.00
ATOM     16  C   _2     1       3.044   1.130   0.006  1.00  0.00
ATOM     17  H   _2     1       3.795   1.915   0.023  1.00  0.00
ATOM     18  C   _2     1       3.447  -0.201   0.025  1.00  0.00
ATOM     19  H   _2     1       4.504  -0.442   0.065  1.00  0.00
ATOM     20  C   _2     1       2.487  -1.224  -0.002  1.00  0.00
ATOM     21  H   _2     1       2.776  -2.270   0.014  1.00  0.00
TER
ENDMDL
REMARK    GENERATED BY TRJCONV
TITLE     bifenil in water t=   2.00000
REMARK    THIS IS A SIMULATION BOX
CRYST1   25.748   22.865   22.968  90.00  90.00  90.00 P 1           1
MODEL        3
ATOM      1  C   _2     1       1.139  -0.892  -0.068  1.00  0.00
ATOM      2  C   _2     1       0.001  -1.818  -0.156  1.00  0.00
ATOM      3  C   _2     1      -1.138  -0.894  -0.045  1.00  0.00
```

```
ATOM      4  C    _2     1      -0.743   0.476  -0.075  1.00  0.00
ATOM      5  C    _2     1       0.742   0.478  -0.088  1.00  0.00
ATOM      6  C    _2     1      -2.481  -1.228   0.087  1.00  0.00
ATOM      7  H    _2     1      -2.769  -2.274   0.135  1.00  0.00
ATOM      8  C    _2     1      -3.440  -0.205   0.137  1.00  0.00
ATOM      9  H    _2     1      -4.493  -0.447   0.238  1.00  0.00
ATOM     10  C    _2     1      -3.045   1.125   0.031  1.00  0.00
ATOM     11  H    _2     1      -3.798   1.908   0.037  1.00  0.00
ATOM     12  C    _2     1      -1.684   1.482  -0.081  1.00  0.00
ATOM     13  H    _2     1      -1.406   2.530  -0.154  1.00  0.00
ATOM     14  C    _2     1       1.679   1.487  -0.022  1.00  0.00
ATOM     15  H    _2     1       1.396   2.535  -0.034  1.00  0.00
ATOM     16  C    _2     1       3.041   1.129   0.074  1.00  0.00
ATOM     17  H    _2     1       3.791   1.912   0.124  1.00  0.00
ATOM     18  C    _2     1       3.442  -0.202   0.115  1.00  0.00
ATOM     19  H    _2     1       4.496  -0.446   0.200  1.00  0.00
ATOM     20  C    _2     1       2.485  -1.227   0.038  1.00  0.00
ATOM     21  H    _2     1       2.773  -2.273   0.058  1.00  0.00
TER
ENDMDL
REMARK    GENERATED BY TRJCONV
TITLE     bifenil in water t=   2.00000
REMARK    THIS IS A SIMULATION BOX
CRYST1   25.748   22.865   22.968  90.00  90.00  90.00 P 1           1
MODEL        4
ATOM      1  C    _2     1       1.138  -0.892  -0.046  1.00  0.00
ATOM      2  C    _2     1       0.001  -1.823  -0.099  1.00  0.00
ATOM      3  C    _2     1      -1.138  -0.894  -0.024  1.00  0.00
ATOM      4  C    _2     1      -0.743   0.476  -0.044  1.00  0.00
ATOM      5  C    _2     1       0.742   0.478  -0.057  1.00  0.00
ATOM      6  C    _2     1      -2.485  -1.228   0.064  1.00  0.00
ATOM      7  H    _2     1      -2.772  -2.274   0.099  1.00  0.00
ATOM      8  C    _2     1      -3.445  -0.204   0.090  1.00  0.00
ATOM      9  H    _2     1      -4.500  -0.447   0.154  1.00  0.00
ATOM     10  C    _2     1      -3.046   1.125   0.011  1.00  0.00
ATOM     11  H    _2     1      -3.799   1.909   0.007  1.00  0.00
ATOM     12  C    _2     1      -1.683   1.483  -0.061  1.00  0.00
ATOM     13  H    _2     1      -1.402   2.532  -0.116  1.00  0.00
ATOM     14  C    _2     1       1.679   1.487  -0.003  1.00  0.00
ATOM     15  H    _2     1       1.397   2.536  -0.001  1.00  0.00
ATOM     16  C    _2     1       3.044   1.129   0.054  1.00  0.00
ATOM     17  H    _2     1       3.793   1.915   0.091  1.00  0.00
ATOM     18  C    _2     1       3.446  -0.201   0.068  1.00  0.00
ATOM     19  H    _2     1       4.503  -0.443   0.118  1.00  0.00
ATOM     20  C    _2     1       2.488  -1.225   0.014  1.00  0.00
ATOM     21  H    _2     1       2.776  -2.272   0.021  1.00  0.00
TER
ENDMDL
REMARK    GENERATED BY TRJCONV
TITLE     bifenil in water t=   2.00000
REMARK    THIS IS A SIMULATION BOX
CRYST1   25.748   22.865   22.968  90.00  90.00  90.00 P 1           1
```

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MODEL        5
ATOM      1  C   _2     1       1.139  -0.892  -0.028  1.00  0.00
ATOM      2  C   _2     1       0.001  -1.826  -0.089  1.00  0.00
ATOM      3  C   _2     1      -1.137  -0.894  -0.053  1.00  0.00
ATOM      4  C   _2     1      -0.743   0.476  -0.062  1.00  0.00
ATOM      5  C   _2     1       0.742   0.477  -0.050  1.00  0.00
ATOM      6  C   _2     1      -2.485  -1.228   0.012  1.00  0.00
ATOM      7  H   _2     1      -2.774  -2.275   0.021  1.00  0.00
ATOM      8  C   _2     1      -3.445  -0.205   0.068  1.00  0.00
ATOM      9  H   _2     1      -4.501  -0.449   0.120  1.00  0.00
ATOM     10  C   _2     1      -3.046   1.126   0.058  1.00  0.00
ATOM     11  H   _2     1      -3.796   1.909   0.102  1.00  0.00
ATOM     12  C   _2     1      -1.681   1.484  -0.001  1.00  0.00
ATOM     13  H   _2     1      -1.400   2.533   0.003  1.00  0.00
ATOM     14  C   _2     1       1.680   1.486  -0.061  1.00  0.00
ATOM     15  H   _2     1       1.398   2.534  -0.107  1.00  0.00
ATOM     16  C   _2     1       3.044   1.130   0.012  1.00  0.00
ATOM     17  H   _2     1       3.796   1.915   0.011  1.00  0.00
ATOM     18  C   _2     1       3.445  -0.199   0.091  1.00  0.00
ATOM     19  H   _2     1       4.501  -0.440   0.158  1.00  0.00
ATOM     20  C   _2     1       2.485  -1.224   0.067  1.00  0.00
ATOM     21  H   _2     1       2.775  -2.270   0.102  1.00  0.00
TER
ENDMDL
REMARK    GENERATED BY TRJCONV
TITLE     bifenil in water t=   2.00000
REMARK    THIS IS A SIMULATION BOX
CRYST1   25.748   22.865   22.968  90.00  90.00  90.00 P 1           1
MODEL        6
ATOM      1  C   _2     1       1.139  -0.893   0.028  1.00  0.00
ATOM      2  C   _2     1       0.001  -1.825   0.087  1.00  0.00
ATOM      3  C   _2     1      -1.138  -0.893   0.052  1.00  0.00
ATOM      4  C   _2     1      -0.743   0.476   0.064  1.00  0.00
ATOM      5  C   _2     1       0.742   0.477   0.050  1.00  0.00
ATOM      6  C   _2     1      -2.486  -1.228  -0.014  1.00  0.00
ATOM      7  H   _2     1      -2.773  -2.276  -0.023  1.00  0.00
ATOM      8  C   _2     1      -3.446  -0.205  -0.069  1.00  0.00
ATOM      9  H   _2     1      -4.502  -0.450  -0.120  1.00  0.00
ATOM     10  C   _2     1      -3.044   1.125  -0.058  1.00  0.00
ATOM     11  H   _2     1      -3.795   1.910  -0.104  1.00  0.00
ATOM     12  C   _2     1      -1.681   1.484   0.002  1.00  0.00
ATOM     13  H   _2     1      -1.399   2.533  -0.001  1.00  0.00
ATOM     14  C   _2     1       1.680   1.486   0.060  1.00  0.00
ATOM     15  H   _2     1       1.398   2.534   0.103  1.00  0.00
ATOM     16  C   _2     1       3.044   1.130  -0.013  1.00  0.00
ATOM     17  H   _2     1       3.795   1.914  -0.014  1.00  0.00
ATOM     18  C   _2     1       3.445  -0.199  -0.090  1.00  0.00
ATOM     19  H   _2     1       4.501  -0.440  -0.158  1.00  0.00
ATOM     20  C   _2     1       2.486  -1.224  -0.066  1.00  0.00
ATOM     21  H   _2     1       2.775  -2.270  -0.103  1.00  0.00
TER
ENDMDL
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REMARK    GENERATED BY TRJCONV
TITLE     bifenil in water t=   2.00000
REMARK    THIS IS A SIMULATION BOX
CRYST1   25.748   22.865   22.968  90.00  90.00  90.00 P 1           1
MODEL        7
ATOM      1  C   _2    1      1.138  -0.891   0.053  1.00  0.00
ATOM      2  C   _2    1      0.001  -1.824   0.088  1.00  0.00
ATOM      3  C   _2    1     -1.138  -0.893   0.029  1.00  0.00
ATOM      4  C   _2    1     -0.743   0.475   0.052  1.00  0.00
ATOM      5  C   _2    1      0.742   0.477   0.064  1.00  0.00
ATOM      6  C   _2    1     -2.484  -1.228  -0.065  1.00  0.00
ATOM      7  H   _2    1     -2.771  -2.274  -0.101  1.00  0.00
ATOM      8  C   _2    1     -3.444  -0.205  -0.092  1.00  0.00
ATOM      9  H   _2    1     -4.500  -0.447  -0.161  1.00  0.00
ATOM     10  C   _2    1     -3.046   1.126  -0.016  1.00  0.00
ATOM     11  H   _2    1     -3.798   1.909  -0.020  1.00  0.00
ATOM     12  C   _2    1     -1.682   1.484   0.062  1.00  0.00
ATOM     13  H   _2    1     -1.403   2.532   0.110  1.00  0.00
ATOM     14  C   _2    1      1.679   1.487   0.003  1.00  0.00
ATOM     15  H   _2    1      1.395   2.535  -0.002  1.00  0.00
ATOM     16  C   _2    1      3.044   1.129  -0.058  1.00  0.00
ATOM     17  H   _2    1      3.793   1.914  -0.102  1.00  0.00
ATOM     18  C   _2    1      3.446  -0.201  -0.070  1.00  0.00
ATOM     19  H   _2    1      4.502  -0.444  -0.126  1.00  0.00
ATOM     20  C   _2    1      2.487  -1.225  -0.014  1.00  0.00
ATOM     21  H   _2    1      2.775  -2.272  -0.024  1.00  0.00
TER
ENDMDL
```

Projection of the electronic energy of the ground state singlet FL onto the essential plane as obtained using the above structures and carrying out a cubic spline. Note that because of the symmetry of the plane, only one half has been reported. The difference between the maximum (red) and the minimum (blue) is equal to 1.8 kJoule/mol .
Note also that the same procedure (calculation and spline) has been also adopted for the excited states (vertical) energies and electric dipole moment matrix (both expectation values and transition dipoles) to be used in the MD-PMM calculations (see text).