Supplementary Material (ESI) for *PCCP*

Supporting information for

"An Ab Initio and TD-DFT study of Solvent Effects on the Electronic Spectra of Nile Red"

Patrick Tuck, Robert Mawhinney, Manit Rappon

1. Optimized structures of Nile Red:
   A. Title and model chemistry, **B.** energy (a.u.), **C.** Cartesian coordinates.

A.NR in gas phase rB3LYP/6-31+G(d)

B. -1032.95994748

C.

C	2.76164800	-1.61269900	-0.18483000
C	1.41976900	-1.94317800	-0.21421900
C	0.41626700	-0.96159000	-0.10036900
C	0.84635600	0.37393100	0.04287000
C	2.18257800	0.73576200	0.07137900
C	3.18791000	-0.25707300	-0.04035300
C	-1.42050100	1.06400700	0.11498000
C	-1.80214400	-0.33995300	-0.02600800
C	-3.23817600	-0.64637200	-0.05102400
C	-4.18455600	0.39817100	0.05431600
C	-3.75115900	1.82227700	0.19316600
C	-2.31799500	2.07796700	0.21672700
H	3.49038700	-2.41009500	-0.25422400
H	1.10883600	-2.97885500	-0.31817200
H	2.41671900	1.78892200	0.15851800
H	-1.98719400	3.10633700	0.31958400
O	-0.08454700	1.37209600	0.14727900
N	-0.91583000	-1.29611200	-0.12847000
N	4.52438700	0.07440400	-0.00816700
C	4.97487200	1.43863600	0.27445700
H	4.31163700	1.88960500	1.01993100
H	5.95694000	1.36311000	0.75530900
C	5.57585000	-0.91382300	-0.25804800
H	5.23907700	-1.61421900	-1.02912600
H	6.42625500	-0.37756000	-0.69461800
C	6.03460600	-1.66891700	0.99699600
H	5.21142800	-2.23175900	1.44926000
H	6.83523500	-2.37441800	0.74300600
H	6.42170900	-0.97556600	1.75261300

C	5.07945200	2.33180700	-0.96928800
H	5.78279700	1.90981900	-1.69654500
H	4.11020900	2.44374900	-1.46609700
H	5.43920400	3.32957400	-0.68983700
O	-4.57459200	2.74051300	0.28475500
C	-3.68813200	-1.97335800	-0.17977300
C	-5.55498100	0.10063000	0.02927900
C	-5.98851000	-1.21491100	-0.09803900
H	-5.38625700	-3.28239800	-0.30217100
C	-5.04977000	-2.25342800	-0.20260500
H	-7.05217300	-1.43818200	-0.11661900
H	-2.95424900	-2.76831100	-0.26011400
H	-6.25766000	0.92402800	0.11181300

A.NR in Benzene rB3LYP/6-31+G(d)

B.

-1032.96891891

C.

C	2.76109100	-1.61450800	-0.18876500
C	1.42143500	-1.94653000	-0.21921700
C	0.41572400	-0.96414300	-0.10369900
C	0.84666800	0.37270600	0.04259300
C	2.18068900	0.73698000	0.07263600
C	3.18815100	-0.25636800	-0.04112100
C	-1.42123700	1.05950100	0.11625800
C	-1.80301000	-0.34063700	-0.02798400
C	-3.23811700	-0.64568200	-0.05285100
C	-4.18409900	0.40101100	0.05529000
C	-3.74729300	1.82148100	0.19584100
C	-2.31917500	2.07630600	0.22087800
H	3.48969600	-2.41199900	-0.26187900
H	1.11323500	-2.98415800	-0.32569200
H	2.41380300	1.79037300	0.16555100
H	-1.98400800	3.10459300	0.32667300
O	-0.08799500	1.36832000	0.14942300
N	-0.91316500	-1.29694400	-0.13260300
N	4.52013400	0.07321400	-0.00793700
C	4.97367700	1.44071100	0.26383300
H	4.30658100	1.90339600	0.99829900
H	5.95155200	1.36614300	0.75268300
C	5.57542800	-0.91711300	-0.24607900
H	5.24056300	-1.63019700	-1.00587500
H	6.42273100	-0.38347700	-0.69115800
C	6.03641200	-1.64906700	1.02121400
H	5.21375700	-2.20177100	1.48734500
H	6.83341100	-2.36141700	0.77544600
H	6.42960000	-0.94247000	1.76123700

C	5.09100900	2.31519900	-0.99146300
H	5.80084400	1.88184900	-1.70561600
H	4.12622900	2.42299100	-1.49836300
H	5.45002600	3.31560700	-0.72092100
O	-4.57354900	2.74467900	0.29367600
C	-3.69169400	-1.97189500	-0.18370100
C	-5.55562500	0.10322600	0.03063600
C	-5.99171300	-1.21134400	-0.09878600
H	-5.39130300	-3.28047000	-0.30731600
C	-5.05373700	-2.25096500	-0.20603700
H	-7.05672900	-1.43295000	-0.11692100
H	-2.96149400	-2.77113300	-0.26629000
H	-6.26242500	0.92399600	0.11492900

A.NR in Acetonitrile rB3LYP/6-31+G(d)

B.

-1032.98199856

C.

C	2.76396500	-1.61436700	-0.19205100
C	1.42818200	-1.94952000	-0.22316300
C	0.41790200	-0.96653700	-0.10409200
C	0.84969800	0.37342500	0.04847600
C	2.17986800	0.74185100	0.08054300
C	3.19085900	-0.25178600	-0.03921400
C	-1.41988700	1.05230100	0.12713900
C	-1.80099600	-0.34026000	-0.02692900
C	-3.23337300	-0.64514800	-0.05761700
C	-4.17988800	0.40368400	0.05937300
C	-3.73947800	1.81760400	0.21485600
C	-2.32000300	2.07287000	0.24124100
H	3.49265900	-2.41200600	-0.27565400
H	1.12518300	-2.99009700	-0.33568800
H	2.40920600	1.79613000	0.18702000
H	-1.97697400	3.09991400	0.35514100
O	-0.09097300	1.36348300	0.16166100
N	-0.90408800	-1.29694500	-0.13626600
N	4.51639200	0.07570900	-0.00784400
C	4.97388200	1.45251800	0.22332500
H	4.31235700	1.93930100	0.94687700
H	5.95517800	1.38819300	0.70591800
C	5.57729300	-0.92089800	-0.21337400
H	5.25714100	-1.64747700	-0.96638500
H	6.43129800	-0.39144600	-0.64944000
C	6.01126800	-1.62604700	1.07764800
H	5.18556000	-2.19081700	1.52422900
H	6.82873700	-2.32515300	0.86372600
H	6.36839900	-0.90140200	1.81859000

C	5.08349000	2.28222000	-1.06206500
H	5.78114800	1.81840000	-1.76908100
H	4.11246100	2.38420000	-1.55879000
H	5.45533400	3.28670300	-0.82659400
O	-4.57259100	2.74743300	0.31919300
C	-3.69093500	-1.96988300	-0.20290200
C	-5.55305100	0.10451400	0.02850200
C	-5.99126500	-1.20779300	-0.11539000
H	-5.39175800	-3.27740300	-0.34428800
C	-5.05325700	-2.24778400	-0.23136600
H	-7.05802700	-1.42810500	-0.13817800
H	-2.96512500	-2.77414900	-0.29260800
H	-6.26603600	0.92075500	0.11950500

A. NR in Mix1 rB3LYP/6-31+G(d)

B.

-1032.97467975

C.

C	2.76241700	-1.61434200	-0.18923200
C	1.42449700	-1.94816500	-0.21934900
C	0.41684900	-0.96551100	-0.10292300
C	0.84778700	0.37276400	0.04452300
C	2.18008200	0.73928300	0.07537000
C	3.18935600	-0.25414100	-0.03985200
C	-1.42099900	1.05607200	0.12005300
C	-1.80229800	-0.34128900	-0.02662600
C	-3.23664900	-0.64550600	-0.05394600
C	-4.18267000	0.40239700	0.05697300
C	-3.74401300	1.81998300	0.20326900
C	-2.31957500	2.07470800	0.22754900
H	3.49088600	-2.41177800	-0.26707800
H	1.11903100	-2.98750500	-0.32728500
H	2.41152600	1.79301300	0.17394700
H	-1.98108100	3.10292600	0.33511500
O	-0.08978100	1.36602700	0.15312200
N	-0.90950800	-1.29757700	-0.13253400
N	4.51843200	0.07478200	-0.00762100
C	4.97422100	1.44521600	0.25164000
H	4.30819800	1.91693100	0.98101000
H	5.95230700	1.37326700	0.74019800
C	5.57669100	-0.91673500	-0.23641600
H	5.24935200	-1.63136300	-0.99783600
H	6.42729200	-0.38227200	-0.67373500
C	6.02522700	-1.64433900	1.03752000
H	5.20694300	-2.22302300	1.47957800
H	6.84649300	-2.33323800	0.80547600
H	6.38196100	-0.93224400	1.79064900
C	5.09183400	2.30392900	-1.01418500

H	5.78539000	1.85055500	-1.73190600
H	4.12257300	2.42536500	-1.50978200
H	5.47243500	3.29976000	-0.75678200
O	-4.57274400	2.74689200	0.30044100
C	-3.69258000	-1.97094300	-0.19023900
C	-5.55503700	0.10432500	0.02950200
C	-5.99262000	-1.20922700	-0.10539900
H	-5.39299400	-3.27901800	-0.32106900
C	-5.05484700	-2.24931500	-0.21536800
H	-7.05858800	-1.42989500	-0.12570100
H	-2.96493500	-2.77314100	-0.27519600
H	-6.26509700	0.92288500	0.11578900

A. NR in gas phase rHF/6-31+G(d)

B.

-1026.49037649

C.

C	2.73809500	-1.60465300	-0.16719700
C	1.40136400	-1.92479000	-0.19664200
C	0.41599500	-0.94766300	-0.09292300
C	0.83906100	0.36492500	0.04018200
C	2.16923000	0.72374100	0.06704100
C	3.16449200	-0.26119600	-0.03547000
C	-1.39568200	1.07142000	0.11317700
C	-1.78906700	-0.34531600	-0.02595700
C	-3.23780000	-0.64341000	-0.05132300
C	-4.16540100	0.39199300	0.05268100
C	-3.71993700	1.81253800	0.19090200
C	-2.27683900	2.06607300	0.21269600
H	3.45193100	-2.39985800	-0.22957500
H	1.09515700	-2.95068800	-0.29342500
H	2.39875300	1.76583200	0.14912700
H	-1.95357000	3.08474800	0.31263300
O	-0.08031800	1.35347000	0.13934700
N	-0.93035200	-1.27215400	-0.12079200
N	4.49595500	0.06716700	-0.00705400
C	4.94798400	1.41848400	0.28308700
H	4.29760200	1.86794800	1.02238300
H	5.92019000	1.33983700	0.75625400
C	5.53810400	-0.91104200	-0.27526000
H	5.20008800	-1.60530700	-1.03354000
H	6.37412000	-0.37989200	-0.71591800
C	6.01856400	-1.66327800	0.96596200
H	5.21322300	-2.21936600	1.43213300
H	6.80634200	-2.36314600	0.70066600
H	6.41684300	-0.97616200	1.70581500
C	5.05975800	2.31538900	-0.95016600
H	5.76093900	1.90173900	-1.66815400
H	4.10450900	2.42911700	-1.44967200

H	5.41430000	3.30248600	-0.66647600
O	-4.51266600	2.71172400	0.28097100
C	-3.68794800	-1.95805400	-0.17933900
C	-5.52999500	0.11118100	0.02850700
C	-5.96812700	-1.19120700	-0.09824500
H	-5.38084600	-3.24228500	-0.30108200
C	-5.04152400	-2.22652900	-0.20222000
H	-7.02136900	-1.40659400	-0.11672500
H	-2.97114200	-2.75209000	-0.25916900
H	-6.22439900	0.92540700	0.11014900

A. NR in Benzene rHF/6-31+G(d)

B.

-1026.49883230

C.

C	2.73967200	-1.60473300	-0.17223700
C	1.40419800	-1.92641500	-0.20275100
C	0.41708700	-0.94914800	-0.09625900
C	0.84035000	0.36338400	0.04108400
C	2.16909900	0.72504700	0.06992000
C	3.16668500	-0.25957400	-0.03605200
C	-1.39487600	1.06804500	0.11666300
C	-1.78879300	-0.34649800	-0.02726800
C	-3.23722200	-0.64349900	-0.05358000
C	-4.16424500	0.39355100	0.05451200
C	-3.71506500	1.81067200	0.19746000
C	-2.27622500	2.06462000	0.21990900
H	3.45326000	-2.40010800	-0.23907000
H	1.10069200	-2.95405300	-0.30317400
H	2.39703400	1.76741300	0.15839400
H	-1.95021400	3.08354000	0.32345100
O	-0.08225200	1.35024600	0.14391800
N	-0.92799800	-1.27230400	-0.12519400
N	4.49473200	0.06787500	-0.00704800
C	4.94816400	1.42334500	0.26825200
H	4.29913300	1.88277200	1.00256500
H	5.92052300	1.34837400	0.74101100
C	5.53968300	-0.91377800	-0.26002100
H	5.20839600	-1.61472600	-1.01503600
H	6.37851500	-0.38529000	-0.69777300
C	6.00914600	-1.65378400	0.99232000
H	5.20054700	-2.20838000	1.45513800
H	6.80053200	-2.35415800	0.73966600
H	6.39921200	-0.95904100	1.72948500
C	5.05971700	2.30333600	-0.97680300
H	5.75874000	1.87829300	-1.69026100
H	4.10334800	2.41386100	-1.47543800
H	5.41721800	3.29284100	-0.70566400
O	-4.50972400	2.71412400	0.29162100

C	-3.69017200	-1.95684700	-0.18612900
C	-5.52959000	0.11354800	0.02974200
C	-5.97030400	-1.18800200	-0.10157600
H	-5.38503200	-3.24001600	-0.31209400
C	-5.04466700	-2.22402800	-0.20959300
H	-7.02479600	-1.40161100	-0.12041700
H	-2.97681800	-2.75471900	-0.26928800
H	-6.22745800	0.92559600	0.11432200

A. NR in Acetonitrile rHF/6-31+G(d)

B.

-1026.51072461

C.

C	2.74177600	-1.60537400	-0.17853600
C	1.40779700	-1.92903400	-0.21051600
C	0.41834500	-0.95128900	-0.10090800
C	0.84189800	0.36147900	0.04117800
C	2.16880900	0.72693200	0.07223500
C	3.16935300	-0.25766900	-0.03718200
C	-1.39333500	1.06336400	0.12154900
C	-1.78821300	-0.34763500	-0.02984200
C	-3.23593100	-0.64332300	-0.05803700
C	-4.16191700	0.39584700	0.05837300
C	-3.70752500	1.80764700	0.21121800
C	-2.27529100	2.06264200	0.23261400
H	3.45449800	-2.40187800	-0.25247900
H	1.10838600	-2.95933000	-0.31592500
H	2.39355300	1.77033900	0.16969900
H	-1.94439200	3.08144500	0.34228900
O	-0.08472200	1.34589100	0.14844700
N	-0.92455800	-1.27225500	-0.13174100
N	4.49315300	0.06880700	-0.00709200
C	4.94806000	1.43121100	0.24006900
H	4.29955600	1.90903500	0.96298800
H	5.92051200	1.36463000	0.71319200
C	5.54232000	-0.91857500	-0.23136500
H	5.22174100	-1.63363300	-0.97759000
H	6.38624300	-0.39615000	-0.66578300
C	5.99322000	-1.63413700	1.04137500
H	5.17901600	-2.18497100	1.49960100
H	6.79049200	-2.33588900	0.81253600
H	6.36945600	-0.92443800	1.77158700
C	5.05988700	2.27956600	-1.02636700
H	5.75590300	1.83399500	-1.73024300
H	4.10180200	2.38295400	-1.52406500
H	5.42188200	3.27360900	-0.77897700
O	-4.50570800	2.71649700	0.31557900
C	-3.69275100	-1.95468500	-0.20018500

C	-5.52854200	0.11704900	0.03220900
C	-5.97282200	-1.18290400	-0.10876200
H	-5.39061200	-3.23599800	-0.33536400
C	-5.04852800	-2.21985300	-0.22515100
H	-7.02918900	-1.39437300	-0.12864800
H	-2.98417000	-2.75788700	-0.29011100
H	-6.23105500	0.92600600	0.12311100

A. NR in Mix1 rHF/6-31+G(d)

B.

-1026.50414470

C.

C	2.74050700	-1.60437500	-0.17600500
C	1.40579700	-1.92708700	-0.20746400
C	0.41751000	-0.94976300	-0.09941600
C	0.84081000	0.36284500	0.04020500
C	2.16869700	0.72636200	0.07053400
C	3.16781700	-0.25814700	-0.03671300
C	-1.39464000	1.06616000	0.11733100
C	-1.78887200	-0.34700300	-0.02897100
C	-3.23701400	-0.64351000	-0.05496800
C	-4.16361200	0.39462400	0.05546600
C	-3.71217000	1.80970700	0.20000600
C	-2.27621400	2.06407200	0.22255500
H	3.45388600	-2.39992300	-0.24555100
H	1.10423100	-2.95593500	-0.31015400
H	2.39523400	1.76905500	0.16305600
H	-1.94819000	3.08310800	0.32798500
O	-0.08379300	1.34844300	0.14506500
N	-0.92665500	-1.27214200	-0.12870400
N	4.49399500	0.06834400	-0.00606000
C	4.94915500	1.42556500	0.26211200
H	4.29950000	1.89136700	0.99168000
H	5.92047200	1.35189900	0.73693400
C	5.54047300	-0.91514500	-0.25104800
H	5.21331800	-1.61906800	-1.00497100
H	6.38150600	-0.38792600	-0.68575700
C	6.00192900	-1.64977400	1.00718800
H	5.18688000	-2.19092000	1.47494700
H	6.78408800	-2.36199300	0.75912800
H	6.40160300	-0.95350800	1.73778100
C	5.06375600	2.29567800	-0.98937300
H	5.76400100	1.86471900	-1.69806700
H	4.10789500	2.40346100	-1.49002700
H	5.42130400	3.28682500	-0.72445500
O	-4.50836100	2.71565400	0.29771900
C	-3.69169400	-1.95622800	-0.18918000
C	-5.52950400	0.11501900	0.03138600

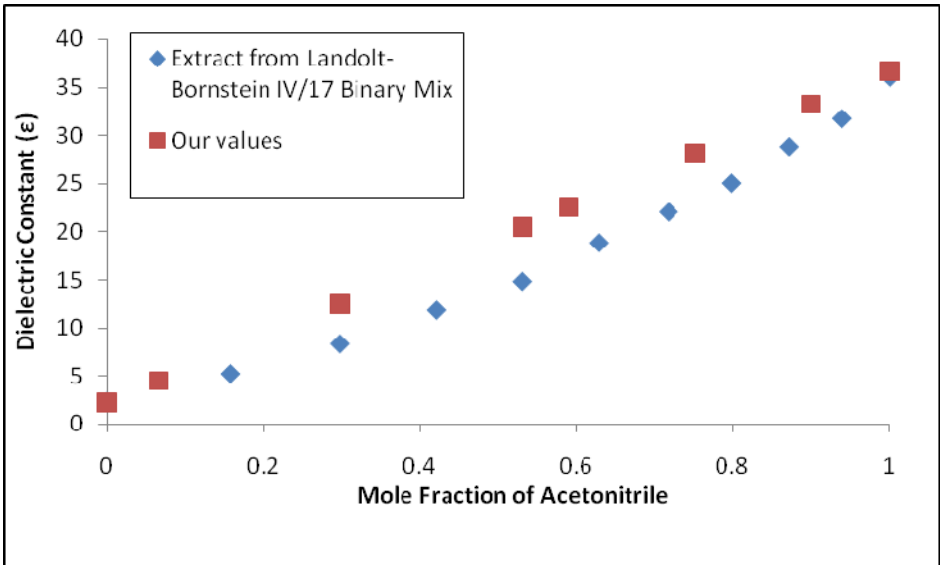
C	-5.97179300	-1.18611200	-0.10157000
H	-5.38785200	-3.23895100	-0.31574100
C	-5.04675200	-2.22267400	-0.21194900
H	-7.02711500	-1.39881700	-0.11984400
H	-2.98049300	-2.75657500	-0.27424700
H	-6.22954900	0.92572200	0.11762300

2. PCM Solvent Specifications

Table of solvent parameters used in the PCM model.

Mixture	**EPS (ε)**	**EPSINF**	**RSOLV**
Gas Phase	N/A	N/A	N/A
Benzene (default values)	2.247	2.244	2.630
Binary Mix 1	4.520	2.215	2.599
Binary Mix 2	12.496	2.113	2.488
Binary Mix 3	20.508	2.011	2.378
Binary Mix 4	22.526	1.986	2.350
Binary Mix 5	28.082	1.915	2.273
Binary Mix 6	33.171	1.850	2.203
Acetonitrile (default values)	36.640	1.806	2.155

Figure S1. Comparison of the relationships between the dielectric constant for the various solvent mixtures and the mole fraction of acetonitrile.



3. Experimental Emission Values

Solvent (ε)	$\lambda_{em\text{-}CIS}$	$\lambda_{em\ exp't}$‡	$\lambda_{em\ exp't} - \lambda_{em\text{-}CIS}$
Gas Phase (0)	308	N/A	N/A
Benzene (2.247)	371	570	199
Binary Mixture 1 (4.52)	376	584	208
Binary Mixture 2 (12.50)	379	598	219
Binary Mixture 3 (20.51)	379	604	225
Binary Mixture 4 (22.53)	379	607	228

Binary Mixture 5 (28.08)	378	609	231
Binary Mixture 6 (33.17)	378	609	231
Acetonitrile (36.64)	377	609	232

‡Experimental solvent/mixtures were measured using a luminescence spectrometer.