Electronic Supporting Information for

Calculation of exchange couplings in the electronically excited state of molecular three-spin systems

Michael Franz,[1] Frank Neese,[2] Sabine Richert [1*]

[1] *Institute of Physical Chemistry, University of Freiburg, Albertstraße 21, 79104 Freiburg, Germany*
[2] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,*
45470 Mülheim an der Ruhr, Germany

* E-mail: sabine.richert@physchem.uni-freiburg.de

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1 Input files

This section shows the input files used in this work for all calculations. The geometry optimisations, on the def2-SVP level of theory, were performed with the following Gaussian input file:

```
%ProcShared=16
%Mem=38gb
#p B3LYP/Def2SVP opt=tight freq int=ultrafine

0,2
some coordinates
```

All TDDFT calculations were carried out using the following ORCA input file:

```
! UKS CAM-B3LYP RIJCOSX def2-TZVP def2/J
! XYZFile TightSCF

%scf
MaxIter 1500
end

%maxcore 20000

%pal nprocs 16
end

%tddft
nroots 40
end

* xyz 0 2
some coordinates
*
```

All CASSCF/QD-NEVPT2 calculations were performed using the following ORCA input file:

```
!RI-JK def2-TZVP NormalPrint MOREAD XYZFILE

%moinp "OrbitalsFromTheTDDFTCalculation.gbw"

%maxcore 20000

%pal nprocs 16
end

%basis
auxC "def2/JK"
auxJK "def2/JK"
end

%casscf
trafostep ri
nel 3
norb 3
mult 4,2
nroots 1,4
PrintWF det
ActOrbs LocOrbs
PTMethod SC_NEVPT2
PTSettings
QDType QD_VanVleck end
end

* xyz 0 2
some coordinates
*
```

2 Benchmark results

For this benchmark, we calculated the exchange interaction J_{TR} for two perylene diimide (PDI) derivatives, which are linked to **BPNO** radicals. We used different approaches, including restricted open-shell CIS (ROCIS) and CASSCF with and without a QD-NEVPT2 correction. The results can be seen in Figure S1. The CASSCF/QD-NEVPT2 calculation yielded the most reliable results.
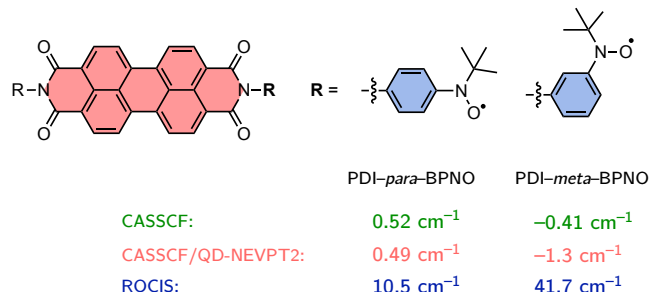

	PDI–*para*–BPNO	PDI–*meta*–BPNO
CASSCF:	0.52 cm^{-1}	−0.41 cm^{-1}
CASSCF/QD-NEVPT2:	0.49 cm^{-1}	−1.3 cm^{-1}
ROCIS:	10.5 cm^{-1}	41.7 cm^{-1}

Figure S1: Calculated exchange interactions for two perylene diimide derivatives using different methods.

3 Exchange interactions J_{TR} for the radical series

Figure S2 shows the calculated exchange interactions J_{TR} for the structures of the radical series. As can be seen, the exchange interactions calculated with the def2-TZVP optimised structures are smaller in magnitude than the exchange interactions calculated with the def2-SVP optimised structures, except for the **perylene−TEMPO** system.
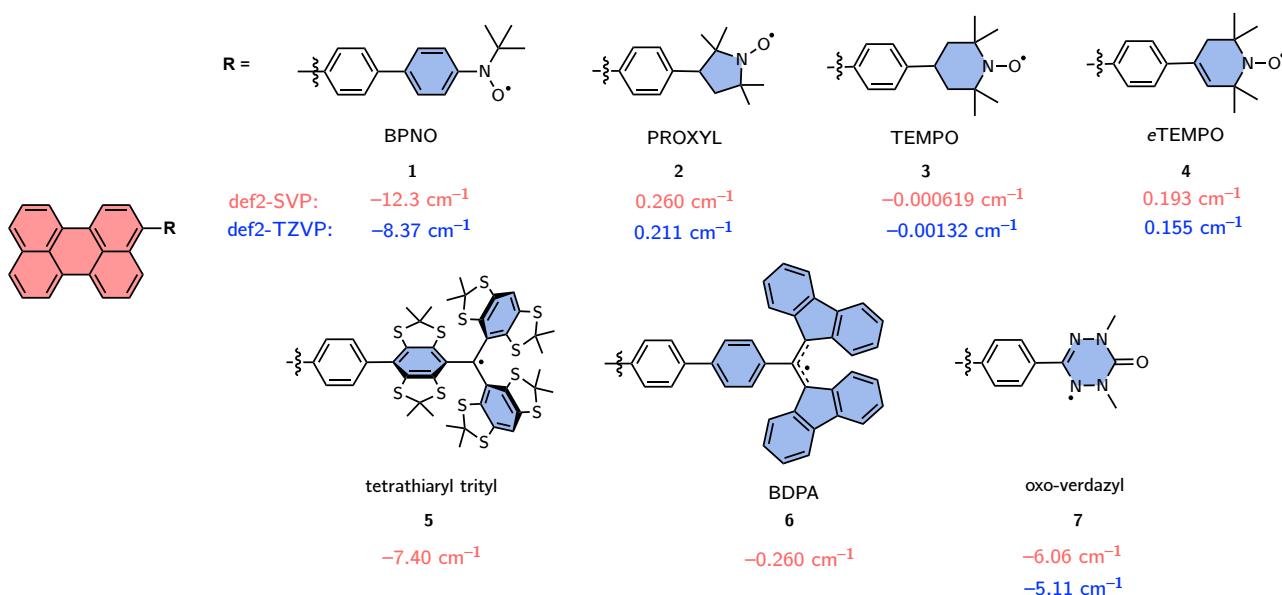

Figure S2: Calculated exchange interactions for the structures of the radical series.

4 Exchange interactions J_{TR} for the linker series

Figure S3 shows the calculated exchange interactions J_{TR} for the structures of the linker series. We varied the linker length in the **perylene−BPNO** and **−BDPA** systems using the def2-SVP basis set for the optimisation of the structures. The calculations predict a reduction in the exchange interaction with increasing length of the phenyl linker.
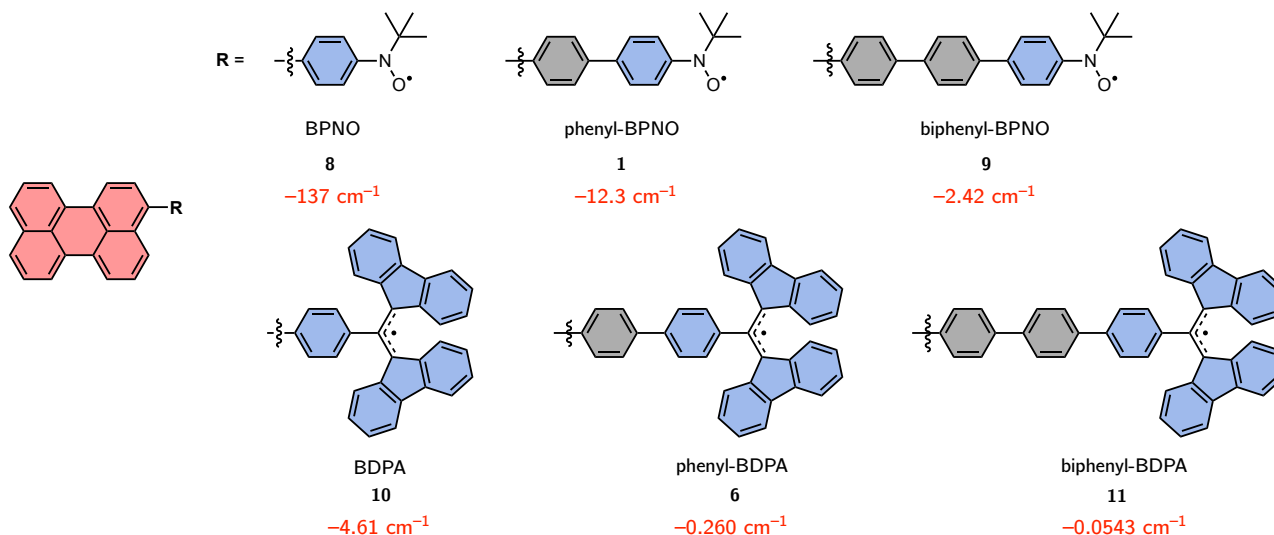

Figure S3: Calculated exchange interactions for the structures of the linker series.

5 Projection of the target states onto the model space

Here we demonstrate how the target states are projected onto the model space. The starting point is the output file with the energies and wavefunctions of the excited states. As an example, we consider the **perylene−phenyl−BPNO** system **1**. The relevant part of the output can be seen below.

The choice of the target states is not necessarily trivial. Normally the states with the largest coefficients with respect to the model space are taken as target states. In our case, that would include the ground state, which would not be meaningful for the description of the three-center-three-electron problem. Furthermore, the coefficients of the neutral determinants for the ground state would presumably vanish as the active space is increased. Thus, the quartet state and the two doublet states ("Root 1" and "Root 2") come into question. When projecting onto the model space (i.e. the neutral determinants), all ionic determinants are omitted and only the neutral determinants have to be normalised.

```
==============================================================
                 QD-NEVPT2 Results
                   (Van Vleck)
==============================================================
 ********************
  MULT 4
 ********************

  Total Hamiltonian to be processed
             0
    0    -1515.341724


 --------------------------
           ROOT = 0
 --------------------------
 --- Reading QDVector (MULT= 4, ROOT= 0) Norm = 1.00000000e+00
  [uuu]    1.000000000

            Total Energy Correction : dE = -6.08431548657813
            Zero Order Energy       : E0 = -1509.25740828230096
            Total Energy (E0+dE)    : E  = -1515.34172376887909


 ********************
  MULT 2
 ********************

  Total Hamiltonian to be processed
             0          1          2          3
    0    -1515.407944  -0.000026  -0.001049   0.007151
    1      -0.000019 -1515.341808  -0.000004  -0.000055
    2      -0.000945   0.000003 -1515.321564   0.000961
    3       0.005029  -0.000035   0.000838 -1515.310913


 --------------------------
           ROOT = 0
 --------------------------
 --- Reading QDVector (MULT= 2, ROOT= 0) Norm = 1.00000000e+00
  [u20]   -0.471431674
  [duu]   -0.000435431
  [udu]    0.536157381
  [uud]   -0.535721951
  [u02]   -0.450838737

            Total Energy Correction : dE = -6.06244648538109
            Zero Order Energy       : E0 = -1509.34589122379043
            Total Energy (E0+dE)    : E  = -1515.40833770917152


 --------------------------
           ROOT = 1
 --------------------------
 --- Reading QDVector (MULT= 2, ROOT= 1) Norm = 1.00000000e+00
  [duu]    0.816401946
  [udu]   -0.408598434
  [uud]   -0.407803512

            Total Energy Correction : dE = -6.08434908833829
            Zero Order Energy       : E0 = -1509.25745852342243
            Total Energy (E0+dE)    : E  = -1515.34180761176071


 --------------------------
           ROOT = 2
 --------------------------
 --- Reading QDVector (MULT= 2, ROOT= 2) Norm = 1.00000000e+00
  [u20]    0.740014737
  [duu]    0.000151312
  [udu]    0.043751505
  [uud]   -0.043902817
  [u02]   -0.669626492

            Total Energy Correction : dE = -6.13164611380080
            Zero Order Energy       : E0 = -1509.18996838288626
            Total Energy (E0+dE)    : E  = -1515.32161449668706


 --------------------------
           ROOT = 3
 --------------------------
 --- Reading QDVector (MULT= 2, ROOT= 3) Norm = 1.00000000e+00
  [u20]    0.479582253
  [duu]    0.001346042
  [udu]    0.458460048
  [uud]   -0.459806090
  [u02]    0.590100506

            Total Energy Correction : dE = -6.21308069496786
            Zero Order Energy       : E0 = -1509.09738841370586
            Total Energy (E0+dE)    : E  = -1515.31046910867371
```

6 Individual exchange interactions

Table S1: Individual exchange interactions of the investigated molecular systems. The subscripts 1, 2 and 3 refer to the HOMO of the chromophore, the radical SOMO, and the chromophore LUMO. Structures optimised with the def2-TZVP basis set are marked with the superscript '*'.

Molecule	J_{12}	J_{13}	J_{23}
1	−25.6	6865	1.11
1*	−27.3	7173	10.6
2	0.916	6803	−0.396
2*	0.779	7140	−0.356
3	−0.113	6798	0.112
3*	−0.0854	7136	0.0828
4	0.645	6796	−0.259
4*	0.569	7110	−0.259
5	−14.7	6761	−0.057
6	18.0	6107	−18.5
7	121	6604	−132
7*	64.2	6915	−73.5
8	−281	7010	11.9
9	−1.47	6819	−3.35
10	21.4	6015	−30.6
11	−1.48	6108	1.37