**Supplementary File**

**THEORETICAL DETERMINATION OF THE ELECTRODE POTENTIAL OF CYANIDIN**

**1. Experimental**

The cyclic voltammogram was recorded on a Voltalab 80 PGZ 402 apparatus, equipped with VoltaMaster 4 software (version 7.0). The following operating conditions have been chosen:

- working electrode: glassy carbon electrode;

- reference electrode: Ag/AgCl/satd. KCl

- supporting electrolyte: MeOH 0.1M NaClO4 (pH=2.35)

- scan rate: 500 mV/s



**Figure 1.** Cyclic voltammogram obtained for the methanolic solution of cyanidin

**2. Computational part**

The intermediate values that have been used for the calculation of ΔGT (see Eqs. (1)-(4) in Methodology) are given below:

**Table 1s.** Values of Gibbs free energies (including thermal corrections and ZPEs (Zero Point Energies)

|  |  |  |
| --- | --- | --- |
| **Compound** | **Gas-phase energies / a.u.** | **Solvent energies / a.u.** |
| Cy\_red 1 | -1023.118992 | -1023.196070 |
| Cy\_red 2 | -1023.119832 | -1023.195989 |
| Cy\_red 3 | -1023.110404 | -1023.189853 |
| Cy\_red 4 | -1023.109500 | -1023.189476 |
| Cy\_red 5 | -1023.111252 | -1023.191810 |
| Cy\_red 6 | -1023.112248 | -1023.191946 |
| Cy\_ox 1 | -1021.952232 | -1022.045650 |
| Cy\_ox 2 | -1021.953428 | -1022.046253 |
| Cy\_ox 3 | -1021.943508 | -1022.037914 |
| Cy\_ox 4 | -1021.953429 | -1022. 046253 |
| Cy\_ox 5 | -1021.952232 | -1022. 045650 |
| Cy\_ox 6 | -1021.953428 | -1022. 046253 |
| 1,2-benzoquinone (Q) | -379.149551 | -379.162770 |
| 1,2-dihydroxybenzene(QH2) | -380.290650 | -380.300895 |

\*1 a.u. = 627.5 kcal mol-1; solvent = methanol

**Table 2s.** Solvation energies (ΔGsol)

|  |  |
| --- | --- |
| **Compound** | **ΔGsol / kcal mol-1** |
| Cy\_red 1 | -48.37 |
| Cy\_red 2 | -47.79 |
| Cy\_red 3 | -49.85 |
| Cy\_red 4 | -50.18 |
| Cy\_red 5 | -50.55 |
| Cy\_red 6 | -50.10 |
| Cy\_ox 1 | -58.62 |
| Cy\_ox 2 | -58.25 |
| Cy\_ox 3 | -59.24 |
| Cy\_ox 4 | -58.25 |
| Cy\_ox 5 | -58.62 |
| Cy\_ox 6 | -58.25 |
| 1,2-benzoquinone (Q) | -8.30 |
| 1,2-dihydroxybenzene(QH2) | -6.43 |