Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Can nitro groups really anchor onto TiO_2? Case study of dye-to-TiO_2 adsorption using azo dyes with NO_2 substituents

Lei Zhang,[ab] *and Jacqueline M. Cole,*[*bcde]

[a] Department of Physics, Nanjing University of Information Science & Technology, Nanjing 210044, China.

[b] Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge, CB3 0HE, UK. E-mail: jmc61@cam.ac.uk

[c] Argonne National Laboratory, 9700 S Cass Avenue, Argonne, IL 60439, USA

[d] ISIS Neutron and Muon Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, OX11 0QX, UK.

[e] Department of Chemical Engineering and Biotechnology, University of Cambridge, Charles Babbage Road, Cambridge, CB3 0FS, UK.

Nitro, Azo, Dye-sensitized solar cell, DFT, TDDFT, Optoelectronic material

Electronic Supplementary Information

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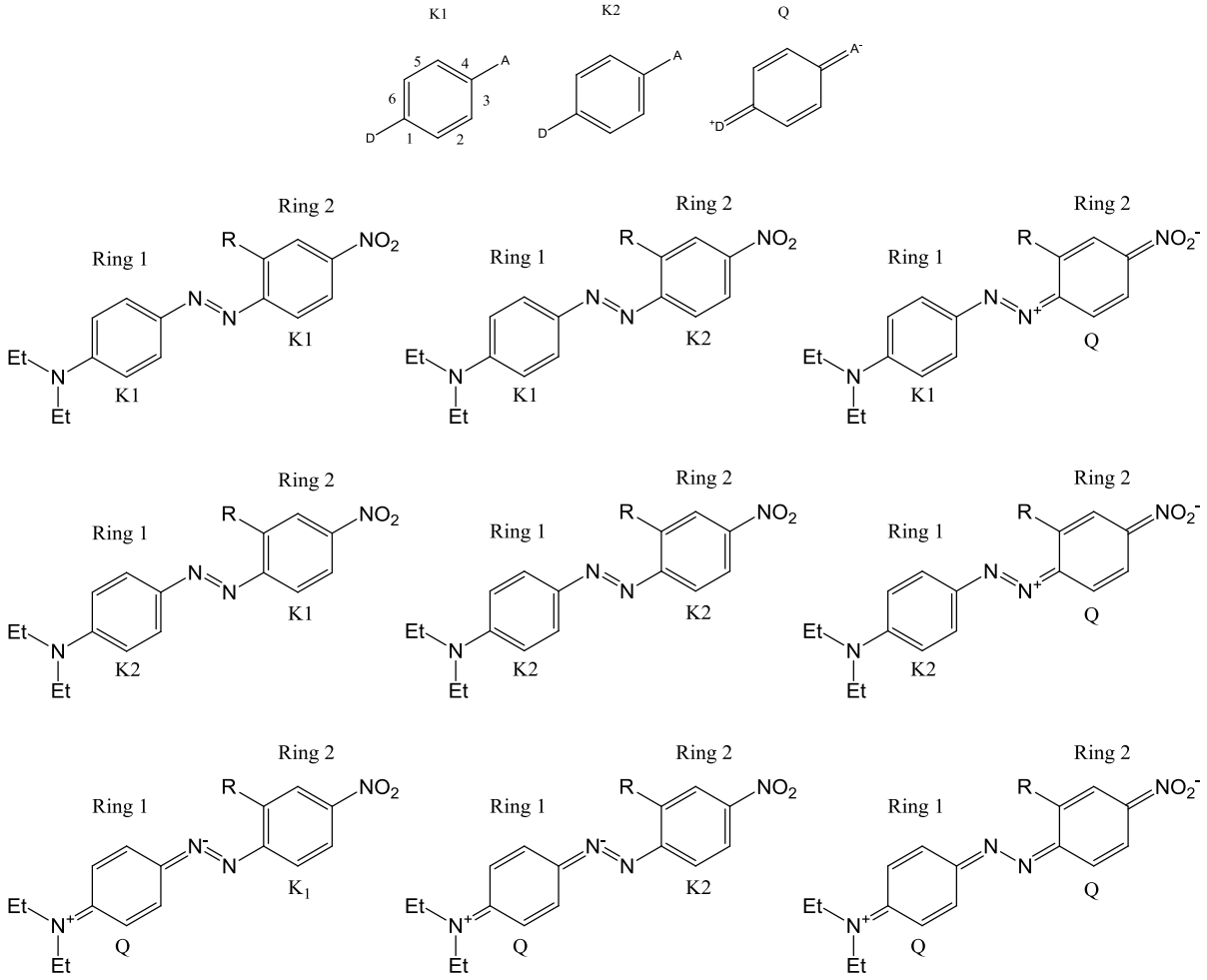
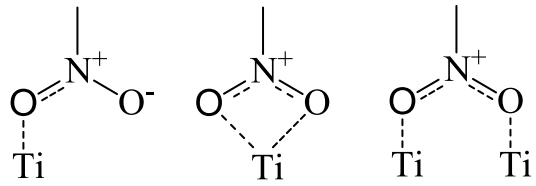
Table S1 Absorption intensity of **1-3** in acetonitrile

	1	**2**	**3**
Molar extinction coefficient ($M^{-1}cm^{-1}$)	6332	16778	41381



Scheme S1 Different resonance states of azo dyes with substituted benzene rings. Q is the quinoidal structure. D is the electron donor while A is the electron acceptor.



Scheme S2 Three inputs for geometrical optimization. From left to right: monodentate, bidentate chelating and bidentate bridging.

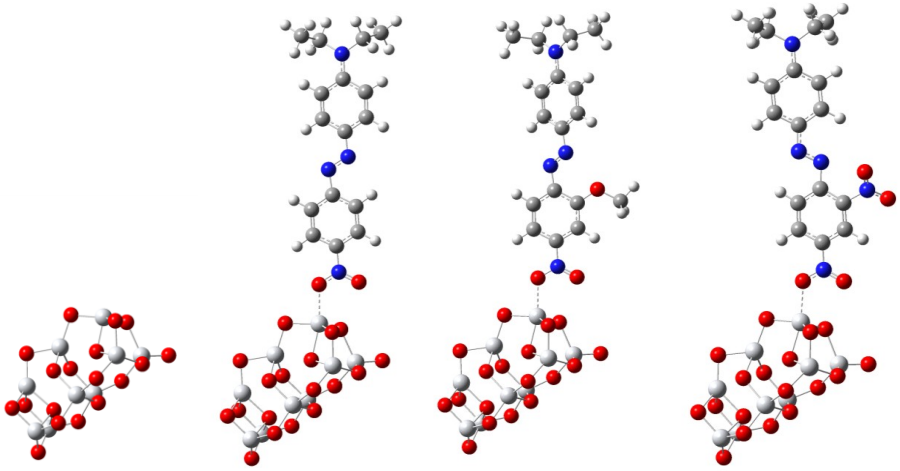


Figure S1 Optimized structures of TiO_2, **1**TiO_2, **2**TiO_2 and **3**TiO_2. All the three inputs (monodentate, bidentate chelating and bidentate bridging) give rise to a monodentate structure in the end, implying that the monodentate adsorption mode affords the best stability for these $–NO_2$ dyes.

Table S2 Electronic transitions of **1**TiO_2, **2**TiO_2 and **3**TiO_2 obtained from TDDFT calculations. H: HOMO. L: LUMO

	Peak wavelength (nm)	Oscillator strength	Major Contributions
1TiO_2	600	0.0070	H-1 to L (0.68)
	572	1.0938	H to L (0.71)
	432	0.0002	H to L+1 (0.71)
	408	0.0005	H to L+2 (0.70)
	398	0.0134	H-2 to L (0.68)
	397	0.0018	H to L+3 (0.70)
2TiO_2	650	0.1657	H-1 to L (0.62), H to L (0.27)
	606	0.8194	H to L (0.66)
	461	0.0001	H to L+1 (0.71)
	445	0.0344	H-2 to L (0.68)
	434	0.0001	H to L+2 (0.70)
	421	0.0003	H to L+3 (0.70)
3TiO_2	621	0.0720	H-1 to L (0.61)
	580	0.9245	H-1 to L (0.29), H to L (0.63)
	423	0.2188	H to L+2 (0.61)
	420	0.0041	H-2 to L (0.67)
	419	0.0008	H to L+1 (0.70)

Table S3 Oxygen to titanium distance (O…Ti distance), diphenyl angle and adsorption energy of **1**TiO_2, **2**TiO_2 and **3**TiO_2.

Compound	O…Ti Distance (Å)	Diphenyl angle (°)	Adsorption energy (eV)
1TiO_2	2.144	2.82	1.28
2TiO_2	2.140	29.83	1.29
3TiO_2	2.160	20.24	1.17

Table S4 Average values and errors for η, J_{sc}, V_{oc} and FF with repeated fabrication and testing.

η

	Fabrication number				
Dye	i	ii	iii	Average	Error
N3	3.68	3.58	3.72	3.63	2%
1	0.03	0.03	0.03	0.03	2%
2	0.03	0.03	0.03	0.03	6%
3	0.04	0.03	-	0.04	12%

J_{sc}

	Fabrication number				
Dye	i	ii	iii	Average	Error
N3	11.96	12.29	11.70	11.98	2%
1	0.14	0.14	0.14	0.14	2%
2	0.16	0.15	0.14	0.15	6%
3	0.18	0.17	-	0.18	4%

V_{oc}

	Fabrication number				
Dye	i	ii	iii	Average	Error
N3	0.69	0.69	0.68	0.67	3%
1	0.36	0.37	0.37	0.37	2%
2	0.38	0.38	0.37	0.38	1%
3	0.40	0.38	-	0.39	3%

FF

	Fabrication number				
Dye	i	ii	iii	Average	Error
N3	0.45	0.43	0.47	0.45	2%
1	0.50	0.50	0.50	0.50	1%
2	0.51	0.51	0.52	0.51	2%
3	0.55	0.50	-	0.53	6%

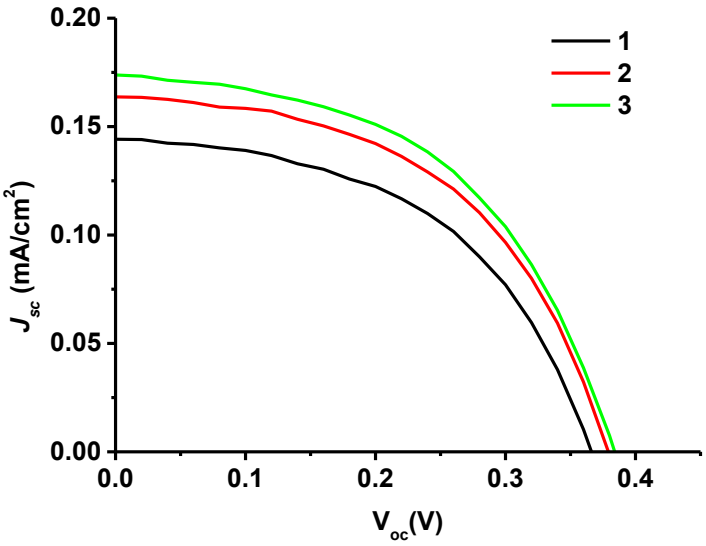


Figure S2 Typical *J-V* curves of these –NO_2 substituted dyes, indicating the capability of the –NO_2 group.

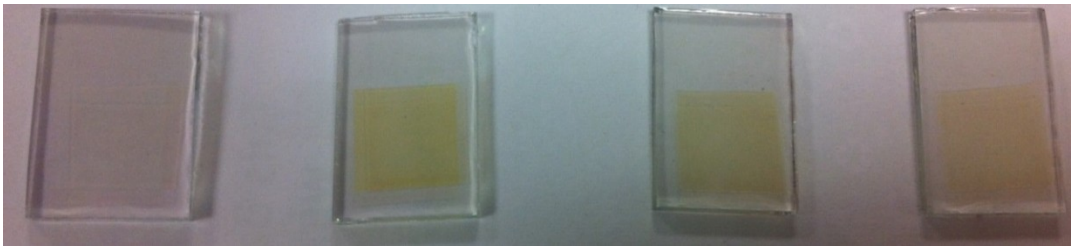


Figure S3 Photos of electrodes after sensitization with the NO_2 dyes compared with pure TiO_2 without sensitization. From left to right: pure TiO_2, **1**TiO_2, **2**TiO_2 and **3**TiO_2.