Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Tuning Photoinduced Processes of Isoalloxazine and Anthraquinone Bichromophores

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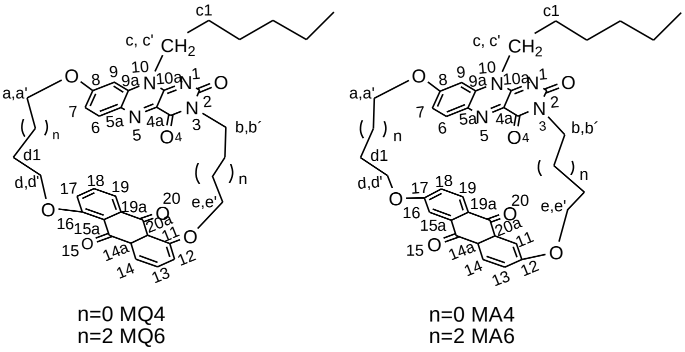


Figure S1- Structures of macrocycles under study

NMR Spectra

MA6 in $CDCl_3$

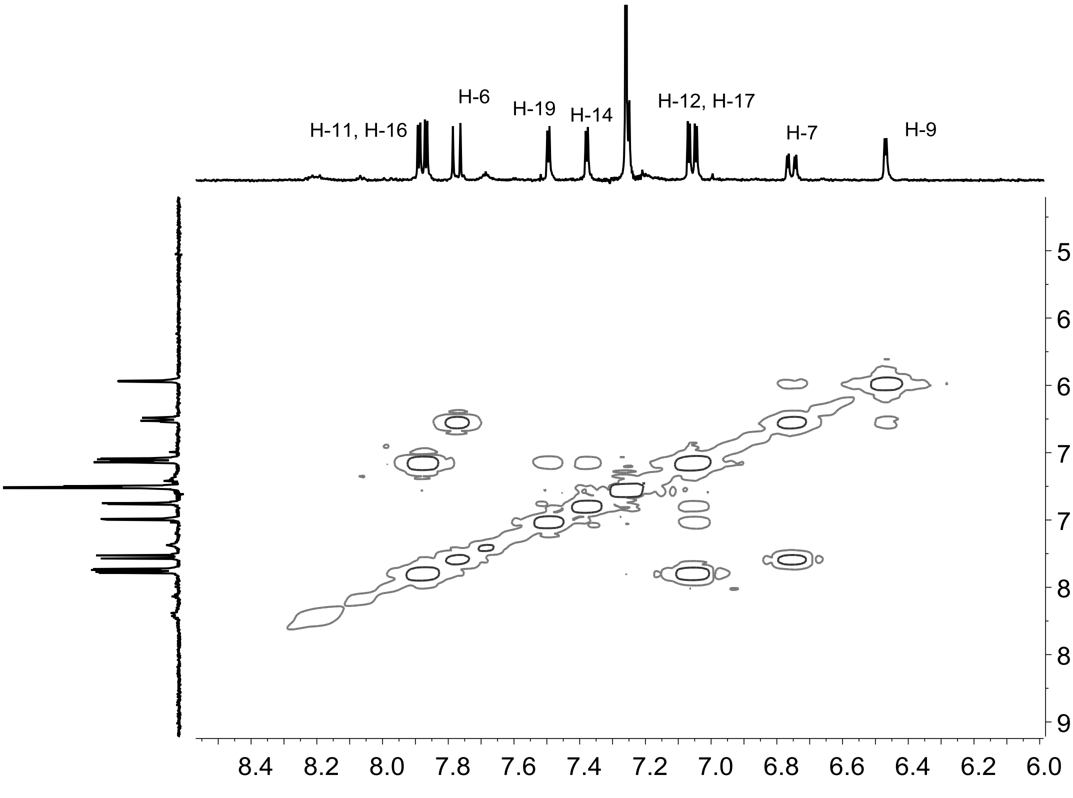


Figure S2- gS-COSY spectra of MA6

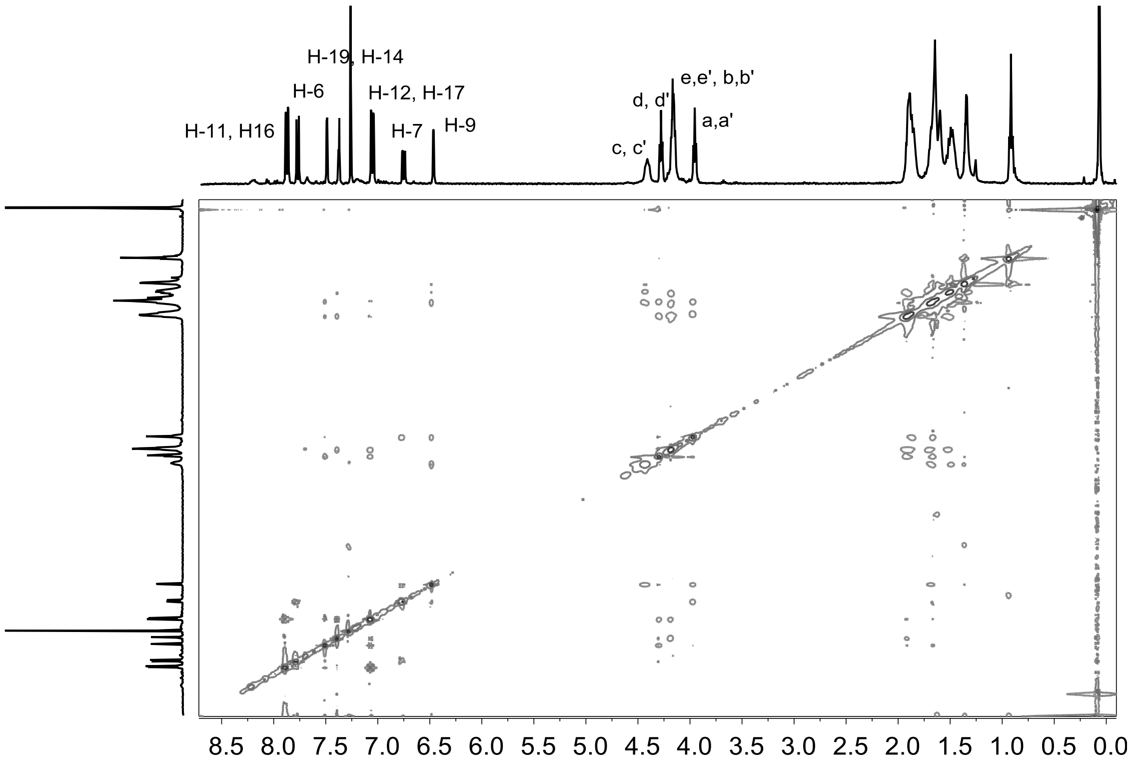


Figure S3 gS-NOESY spectra MA6

MQ6 in $CDCl_3$

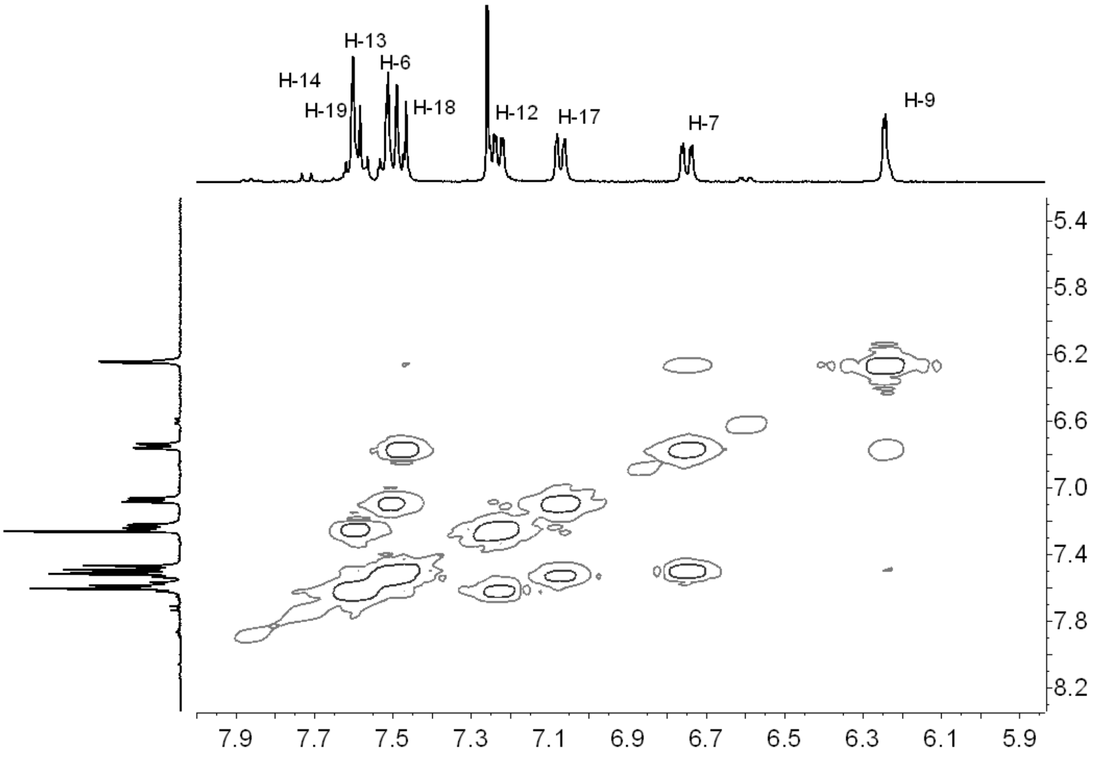


Figure S4. gS-COSY spectra of MQ6

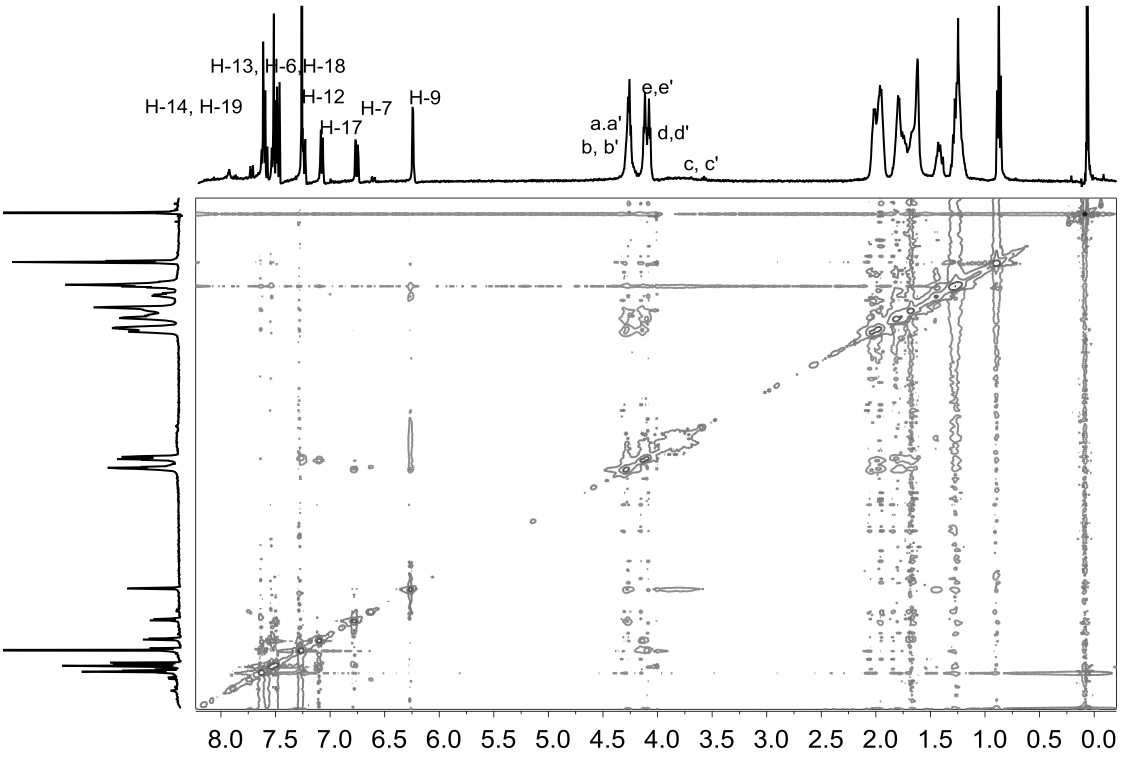


Figure S5. gS-NOESY spectra MQ6

MQ4 in CDCl$_3$

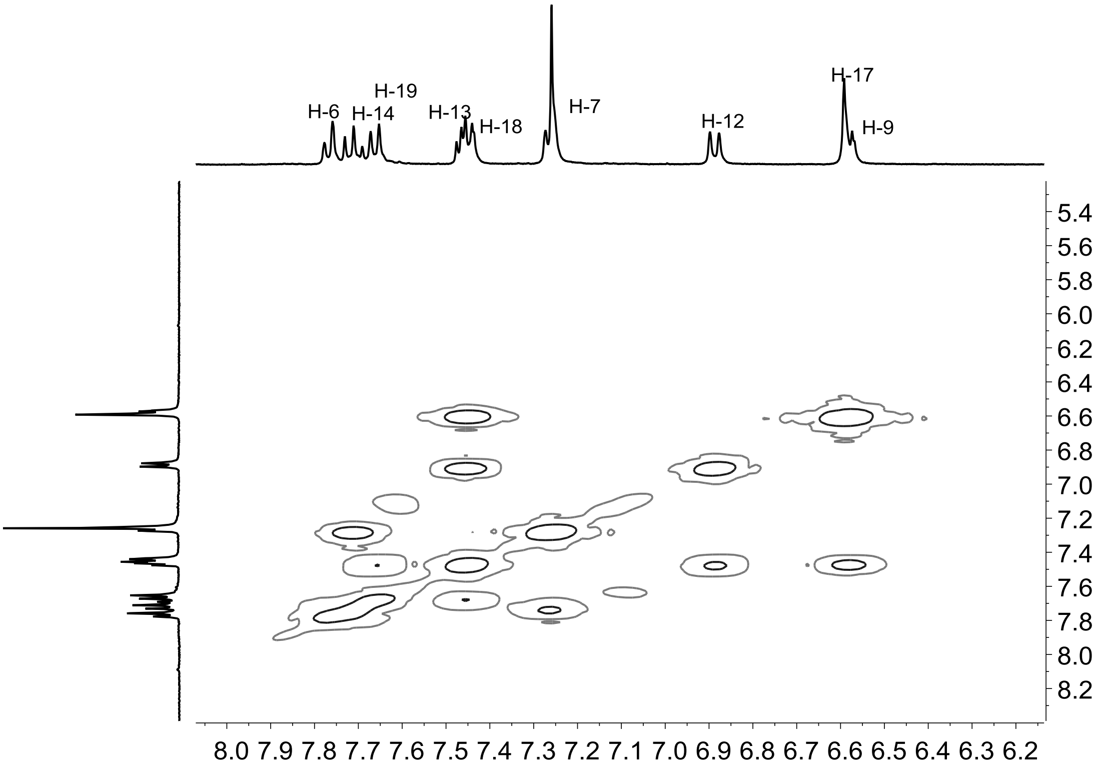


Figure S6. gS-COSY spectra of MQ4

GS-NOESY MQ4

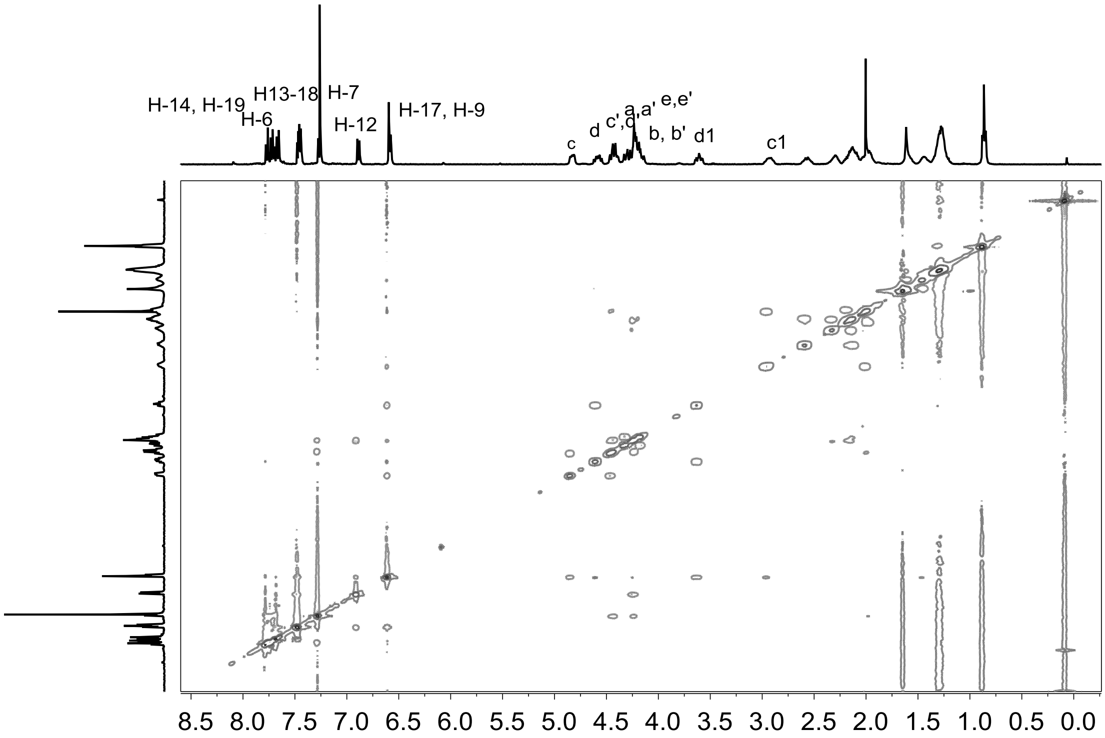


Figure S7. gS-NOESY spectra of MQ4

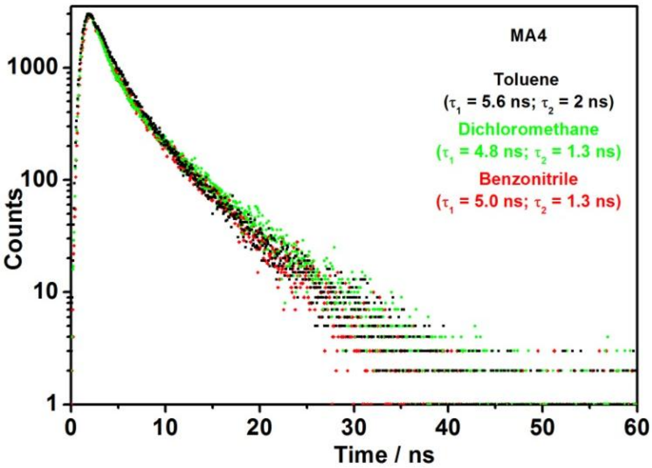


Figure S8-Lifetime measurements of MA4in toluene, dichloromethane and benzonitrile

X –Ray Structures

Experimental data for the X-Ray structure of MQ6
C46 H54 N4 O9, M = 806.93,
Triclinic, space group P-1
a = 13.322(4), b = 13.735(4), c = 14.199(4) A ,
alpha = 67.748(5) deg., beta = 63.947(5) deg., gamma = 64.564(5) deg.,
U = 2049.3(10) A^3 (by least squares refinement on 7140 reflection positions),
T =180(2)K, lambda = 0.71073 A, Z = 2,
D(cal) = 1.308 Mg/m^3, F(000) = 860.
mu(MoK-alpha) = 0.091 mm^-1.
Crystal character:yellow block.

Crystal dimensions 0.38 x 0.30 x 0.22 mm, he crystals were grown by the slow cooling of a concentrated solution of the macrocyclein formamide to give yellow blocks. The asymmetric unit contains the macrocycle and two molecules of formamide.(2 macrocycles and 4 formamides in the unit cell related by an inversion centre)

The hexyl chain of the macrocycle is disordered with an occupation of 3:1. The disorder was traced right back to the first carbon (C44) of the chain.There are two molecules of formamide. The hydrogens on the formamide nitrogens were locatedin a fourier map and their position allowed to refine but with distance restraints and there thermalparameters linked to 1.5times that of the nitrogen they are attached too. They form a hydrogen bonded ribbonthrough the crystal travelling along the c axis of the cell and involve short O..NH dimers and longer(and weaker) O..CH interactions. The quinone carbonyls are bent towards the π-system of the other ring (like a twisted butterfly). Below is a list of the atoms and their deviation from a mean plane through the central pyrazine ring and the distance of the carbonyl C and O of the quinone from that plane. (* atoms used to define plane)

*	-0.0195 (0.0548)	C26
*	0.0294 (0.0809)	N27
*	-0.0178 (0.0514)	C28
*	-0.0035 (0.0099)	C33
*	0.0125 (0.0354)	N34
*	-0.0011 (0.0027)	C35
	3.2883 (9.1972)	C7
	2.9484 (8.2466)	O7
	3.4621 (9.6828)	C14
	3.1833 (8.9027)	O14

with the closest atomic contact between O14 and C28 (3.2103 (0.0027)Angstroms O14 - C28).

The two carbonyl groups jut out of the twisted boat shaped central ring of the quinone and below is their distance from a mean plane through the base of the boat shaped ring defined by C4, C6, C13 and C15 (* atoms used to define plane)

*   0.0604 (0.0009) C4
* -0.0643 (0.0010) C6
*   0.0569 (0.0009) C13
* -0.0530 (0.0009) C15
-0.0661 (0.0040) C7
-0.2598 (0.0058) O7
-0.2552 (0.0030) C14
-0.6771 (0.0045) O14

The angle between the two carbonyl groups and a mean plane defined by these four atoms forming the bottom of the boat shaped central ring of the quinone is
C7=O7 (with approximate esd) = 11.11 (0.15) and
C14=O14 (with approximate esd) = 20.04 (0.15) degrees.

The macrocycles form an infinite π stacking using the internal πstacking between the quinone of the macrocycle and the heterocyclic ring but the inter-macrocyclic π stacking is between similar π- systems. This involves the quinone of one ring and the quinone of a symmetry related ring and the nitrogen heterocycle of one macrocycle and the nitrogen heterocycle of a symmetry realated macrocycle travelling roughly along the ab diagonal of the cell. There is a very good overlap (they are parallel and related by an inversion centre) between the inter-macrocyle π-stacking of the nitrogen heterocycles with a centroid-centroid distance (middle rings) of 3.465A and the closest atomic contact, C30-C37 of 3.380A (measured using Mercury). The π stacking in the quinone is different. Although the rings are parallel, the stacking is only via the overlap of a terminal ring of each anthraquinone. The anthraquinone is beveled having a boat form of the central quinone ring and the π-stacking is an overlap of one of the phenolic rings with a symmetry related one where the two π systems are separated by 3.671A (centroid-centroid distance) with the closest atomic contact C3-C7 (3.275A (Mercury)). There are several hydrogen bonds with the amide hydrogens of the formamide molecules. These are mostly between the formamide molecules but also between O30 and O32 of the
nitrogen heterocycle with the formamides. These are tabulated below with the symmetry operation describing hydrogen bonds to symmetry related molecules.

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.919(18)	2.104(19)	3.017(3)	172(3)	N103-H03A...O201
0.910(17)	2.176(18)	3.080(3)	172(3)	N103-H03B...O30
0.893(17)	2.035(18)	2.926(3)	175(2)	N203-H03C...O101
0.877(16)	2.11(2)	2.931(3)	156(3)	N203-H03D...O32_$1
0.95	2.84	3.713(3)	153.4	C202-H20C...O201_$2

Experimental data for MQ4- X-ray Crystal Structure

The asymmetric unit contains the macrocycle. There are 4 macrocycles in the unit cell. There are some close contacts between some of the carbonyls and nitrogens of the macrocycle and some of the CHs of neighbouring macrocycles. These are tabulated below

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.95	2.37	3.255(3)	154.0	C35-H35A...O14_$2
0.95	2.61	3.548(3)	171.5	C4-H4A...N27_$3
0.95	2.59	3.334(3)	135.9	C4-H4A...O28_$3
0.95	2.53	3.436(3)	159.8	C10-H10A...O30_$4

π-stacking: This is described in terms of closest atomic contact between interacting rings and the angle between mean planes through the interacting rings and the atoms used to define the mean planes.There is intra π-stacking between the anthraquinone and the other ring. Closest atomic contact 3.3736 (0.0032) C7 - C24

Atoms used to define mean planes through the interacting π- systems

C2 C5 C7 C9 C12 C14 and C23 N25 N27 C30 N32 C34

and angle between them 3.38 (0.06) degrees

There is an infinite pi stack travelling along the "a" axis of the cell

Inter π– stacking

Closest atomic contact

3.2067 (0.0028) C14 - O30_$1

Atoms used to define mean planes through the interacting π-systems

C2 C5 C7 C9 C12 C14 and C23 N25 N27 C30 N32 C34

and angle between them is the same as above as it is just a symmetry related ring. The angle between the two π-systems in the macrocycle was measured by defining mean planes through the anthraquinone and a symmetry related anthraquinone and using the same approach to define a mean plane through the other macrocycle and a symmetry related macrocycle. It is 57.03 (0.03) degrees. The symmetry operators used to generate equivalent atoms defined in the above contacts were

$1 x-1, y, z

$2 x, 1/2-y, -1/2+z

$3 -x, 1-y, 1-z

$4 x-1, 1/2-y, -1/2+z

Crystal Data

C38 H38 N4 O7, M = 662.72, Monoclinic, space group P2(1)/c

a = 7.28715(18), b = 29.6837(6), c = 14.4618(4) A ,

alpha = 90 deg., beta = 94.412(2) deg., gamma = 90 deg.,

U = 3118.96(13) A^3 (by least squares refinement on 8204 reflection positions),

T =100(2)K, lambda = 0.71073 A, Z = 4,

D(cal) = 1.411 Mg/m^3, F(000) = 1400.

mu(MoK-alpha) = 0.098 mm^-1.

Crystal character:yellow block.

Crystal dimensions 0.40 x 0.25 x 0.25 mm

Experimental data for MA4

Crystal Data

The crystals were poor and very weakly diffracting. There are A alerts in the cif checker
The asymmetric unit contains two crystallographically independent macrocycles which are very similar.

C38 H38 N4 O7, M = 662.72, Triclinic, space group P-1
a = 14.7145(7), b = 15.4950(8), c = 15.5967(6) A ,
alpha = 72.967(4) deg., beta = 77.681(4) deg., gamma = 71.913(5) deg.,
U = 3202.6(3) A^3 (by least squares refinement on 4703 reflection positions),
T =100(2)K, lambda = 1.54184 A, Z = 4,
D(cal) = 1.374 Mg/m^3, F(000) = 1400.
mu(MoK-alpha) = 0.782 mm^-1.
Crystal character:yellow block.
Crystal dimensions 0.12 x 0.08 x 0.06 mm,
Data Collection and Processing.
Oxford Diffraction Gemini four-circle system with Ruby CCD area detector.
The crystal was held at 100(2)
K with the Oxford Cryosystem Cryostream Cobra.
Maximum theta was 54.41 deg.
The hkl ranges were -15/ 15, -16/ 16, -16/ 16.
15716 reflections measured, 6929 unique [R(int) = 0.0426].
Absorption correction by Semi-empirical from equivalents;
minimum and maximum transmission factors: 0.95, 1.00
no crystal decay

Structure Analysis and Refinement.

No systematic absences. Space group P-1 was chosen on the basis of intensity statistics and shown to be correct by successful refinement. The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The weighting scheme was calculated
w=1/[\s^2^(Fo^2^)+(0.0515P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3.
Goodness-of-fit on F^2 was 0.838,
R1[for 3881 reflections with
I>2sigma(I)] = 0.0451, wR2 = 0.1018.
Data / restraints / parameters 6929/ 0/ 885.

Largest difference Fourier peak and hole 0.478 and -0.275 e.A^-3 .

C38 H38 N4 O7, M = 662.72, Monoclinic, space group P2(1)/c

a = 7.28715(18), b = 29.6837(6), c = 14.4618(4) A ,

alpha = 90 deg., beta = 94.412(2) deg., gamma = 90 deg.,

U = 3118.96(13) A^3 (by least squares refinement on 8204 reflection positions),

T =100(2)K, lambda = 0.71073 A, Z = 4,

D(cal) = 1.411 Mg/m^3, F(000) = 1400.

mu(MoK-alpha) = 0.098 mm^-1.

Crystal character:yellow block.

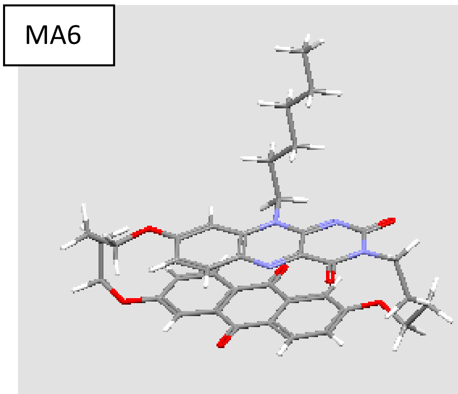
Crystal dimensions 0.40 x 0.25 x 0.25 mm

Molecular Modelling

MM calculations. MacroModel v.8.1, with the GB/SA model for chloroform was used in order to perform the molecular simulations of **MQn** and **MAn** in all cases. All calculations were achieved with Monte Carlo (MC) conformational analyses. Previously to MC all molecules were energy-minimized. Minimisation is carried out using Polak-Ribiere conjugate gradient optimiser. In a typical MC run a MCMM is performed with, at least, 1000 steps for each degree of freedom, this leads to a MC run between 10000-20000 steps. The force field used in these calculations was AMBER as implemented in the version of the programme. The minimised structures have very similar geometry to the X-ray structures solved , proving that the two chromophores are prone to find the maximal amount of π-π interactions intra or intermolecularly. For discussion sake dihedral angles between the perpendicular planes of the central ring of both chromophores have been measured.

Figure S9. MQ4 minimum energy conformation

MA6



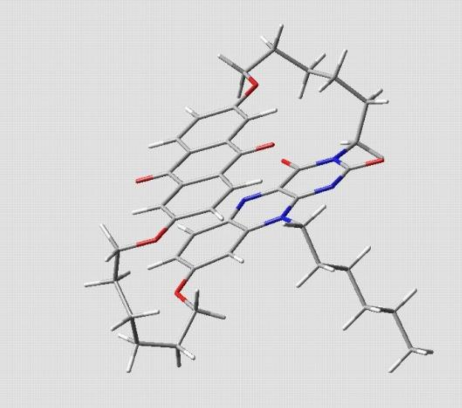


Figure S9. MA4 minimum energy conformation

Figure S10. MA& minimum energy conformation

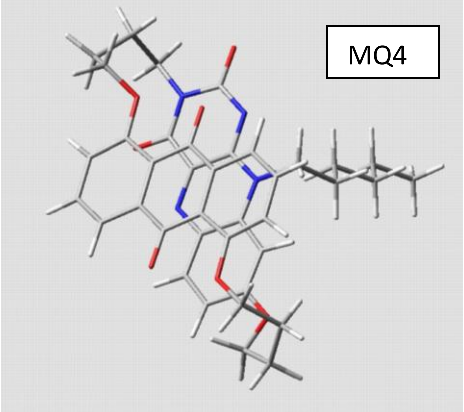


Figure S11. MQ4 minimum energy conformation

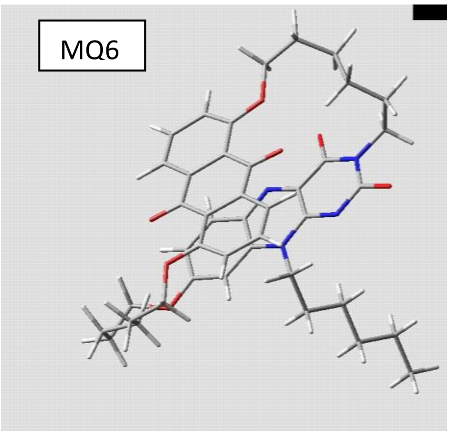


Figure S11. MQ6 minimum energy conformation