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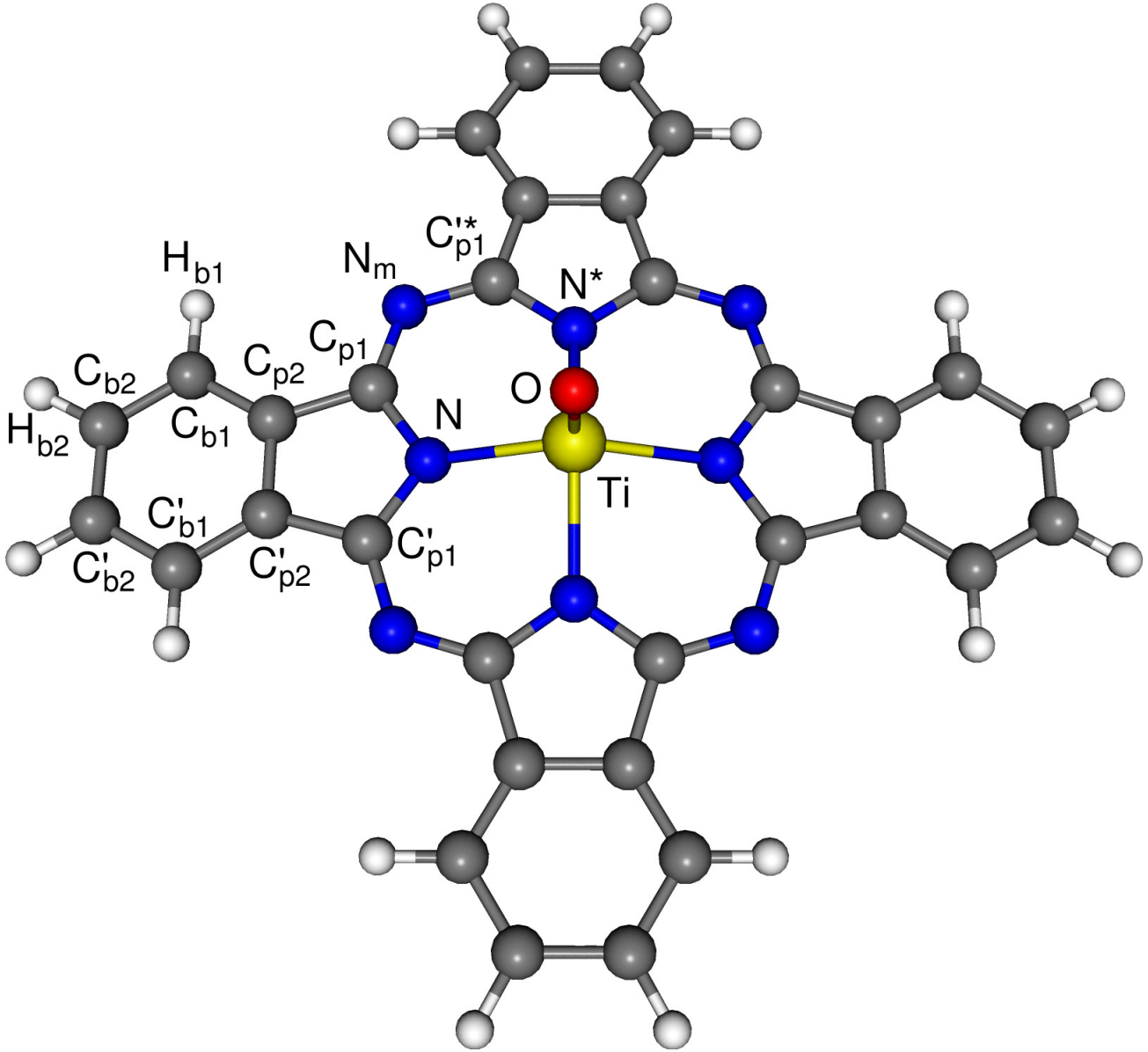
Oxotitanium and dihalogenotitanium porphyrins and phthalocyanines: a density functional theory and gas electron diffraction study

(TiOPc, TiX_2P and TiX_2Pc, where P = porphyrin, Pc = phthalocyanine, X = F, Cl, Br, I)



TiOPc molecule (C_{4v} symmetry) with atom designations

X-Ray crystallographic data

1. W. Hillar, J. Strähle, W. Kovel, and M. Hanack, *Z. Kristallogr.*, 1982, **159**, 173.

Oxotitanium phthalocyanine: polymorphic in the solid state, exists in several crystal modifications, mainly I (β-TiOPc), II (α-TiOPc) and Y, as well as in amorphous form.

Phase I: monoclinic structure in space group $P2_1/c$.
Phase II: triclinic in space group $P\overline{1}$.

Density functional theory calculations

2. A. V. Zakharov and G. V. Girichev, *J. Mol. Struct.: THEOCHEM*, 2008, **851**, 183.

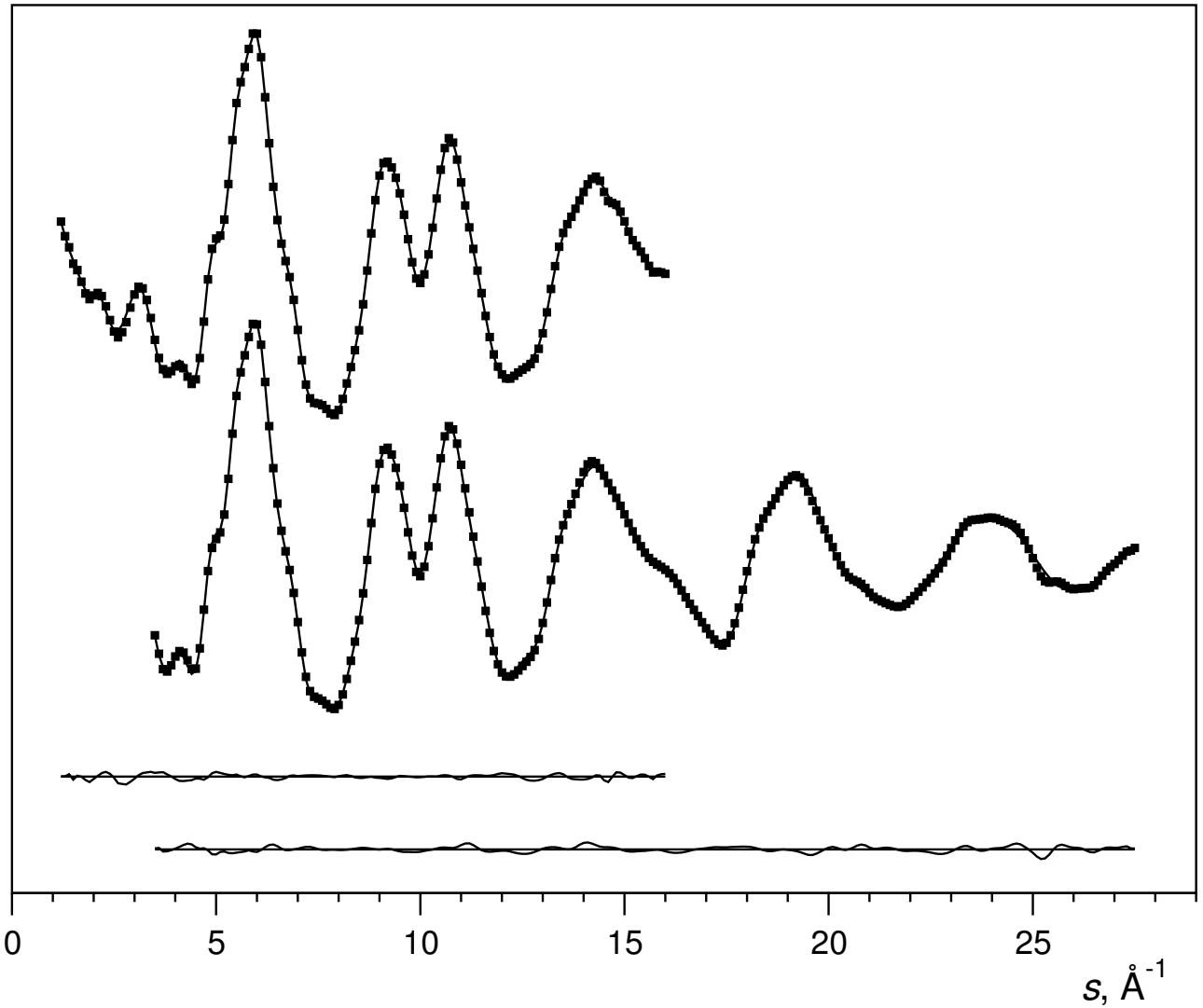
Oxotitanium porphyrin, octamethylporphyrin, porphyrazine and phthalocyanine: equilibrium structures of C_{4v} symmetry with convex macrocycles.

Computational

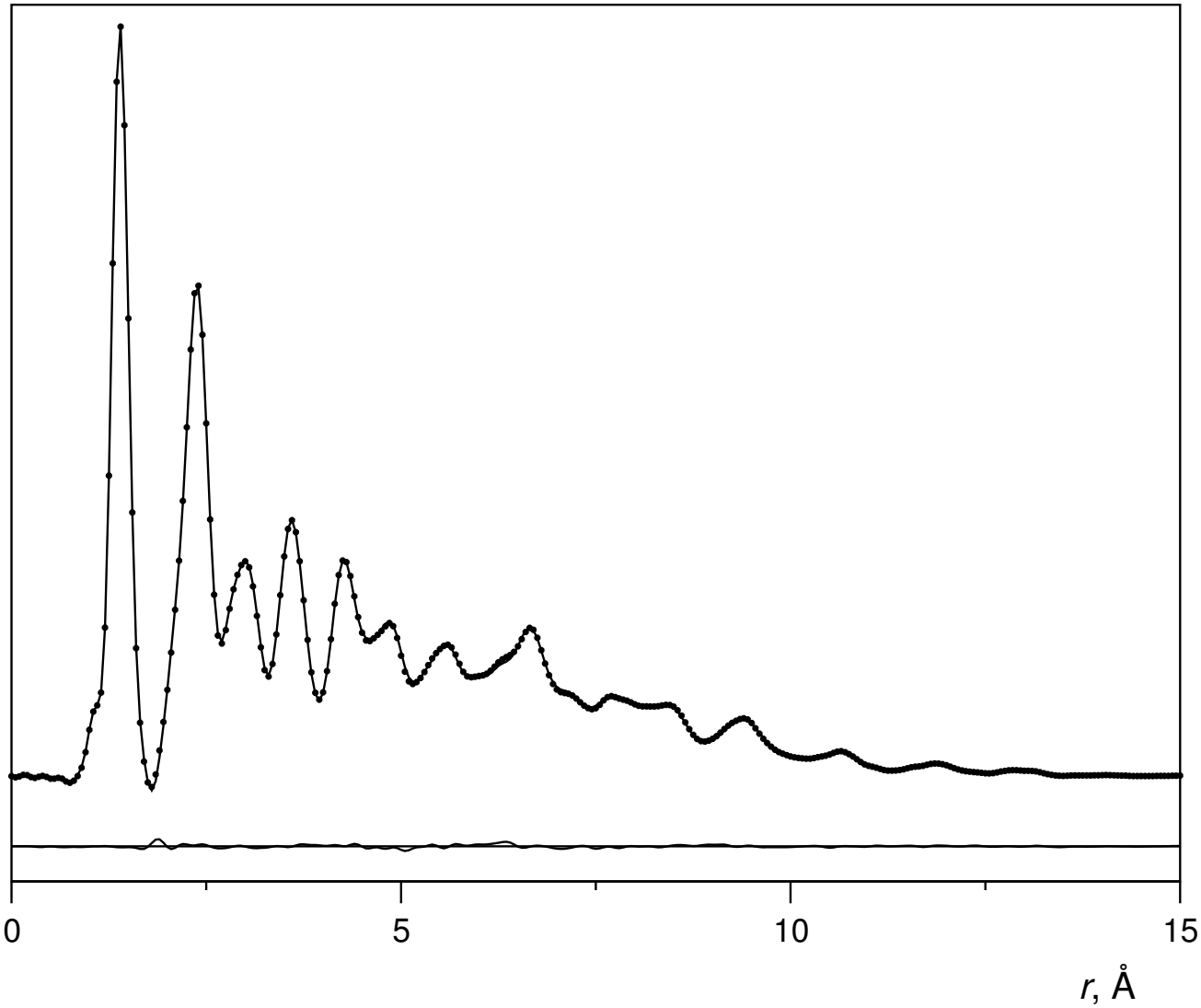
Combination of basis sets 1 (used in study [1])
Ti: $8s7p6d1f/6s5p3d1f$ basis set and RECP (M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866)
C, N, H, O: $10s6p/5s3p$ basis set (T. H. Dunning, *J. Chem. Phys.*, 1971, **55**, 716) with one polarisation d function (C, N, F) or p function (H)

Combination of basis sets 2
Ti: $8s7p6d2f1g/6s5p3d2f1g$ basis set and RECP (M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866; J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408)
C, N, H, O: cc-pVTZ basis sets (J. T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007)

Combination of basis sets 3
Ti: cc-pVTZ-NR (N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2005, **123**, 064107)
C, N, H, O: cc-pVTZ basis sets



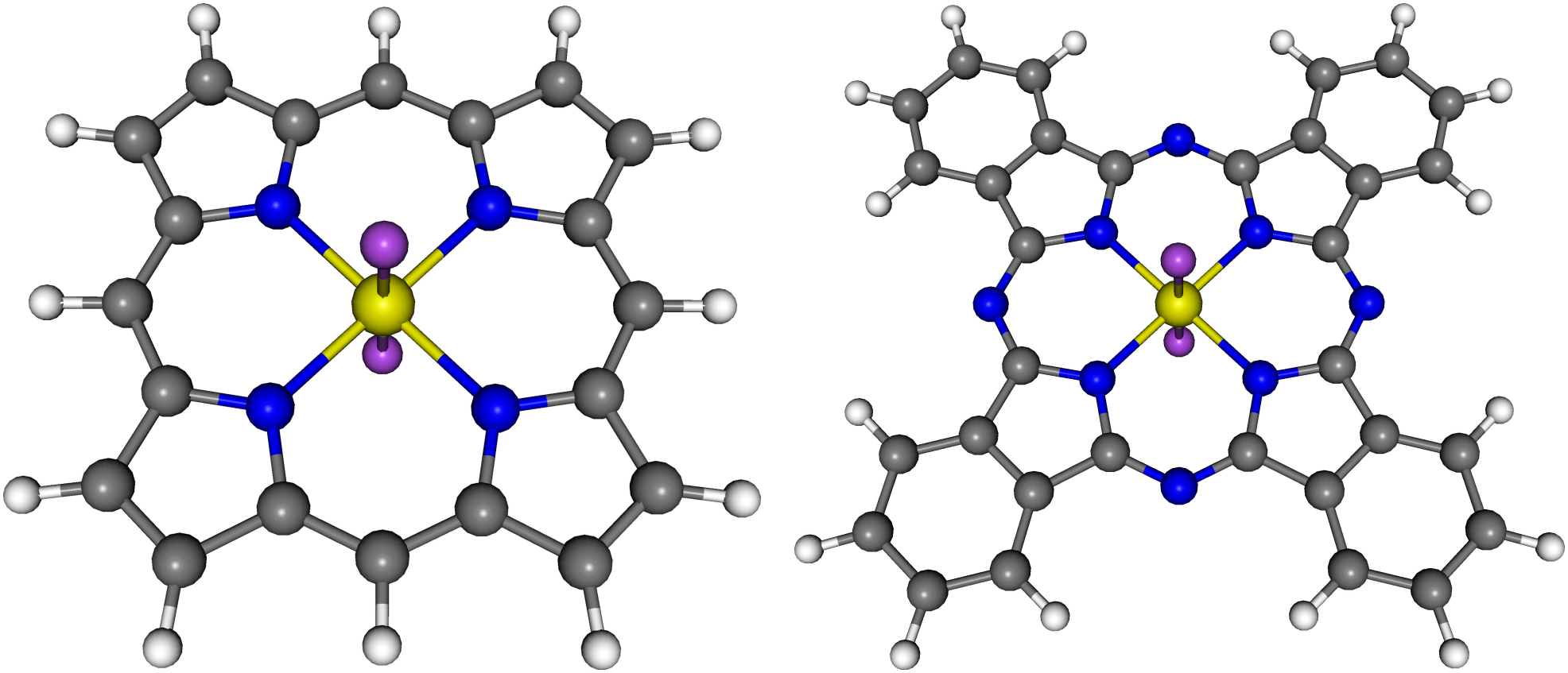
Average experimental (dots) and theoretical (full lines) molecular intensity curves for TiOPc from the long (upper curve) and short (lower curve) camera distances and difference curves (below).



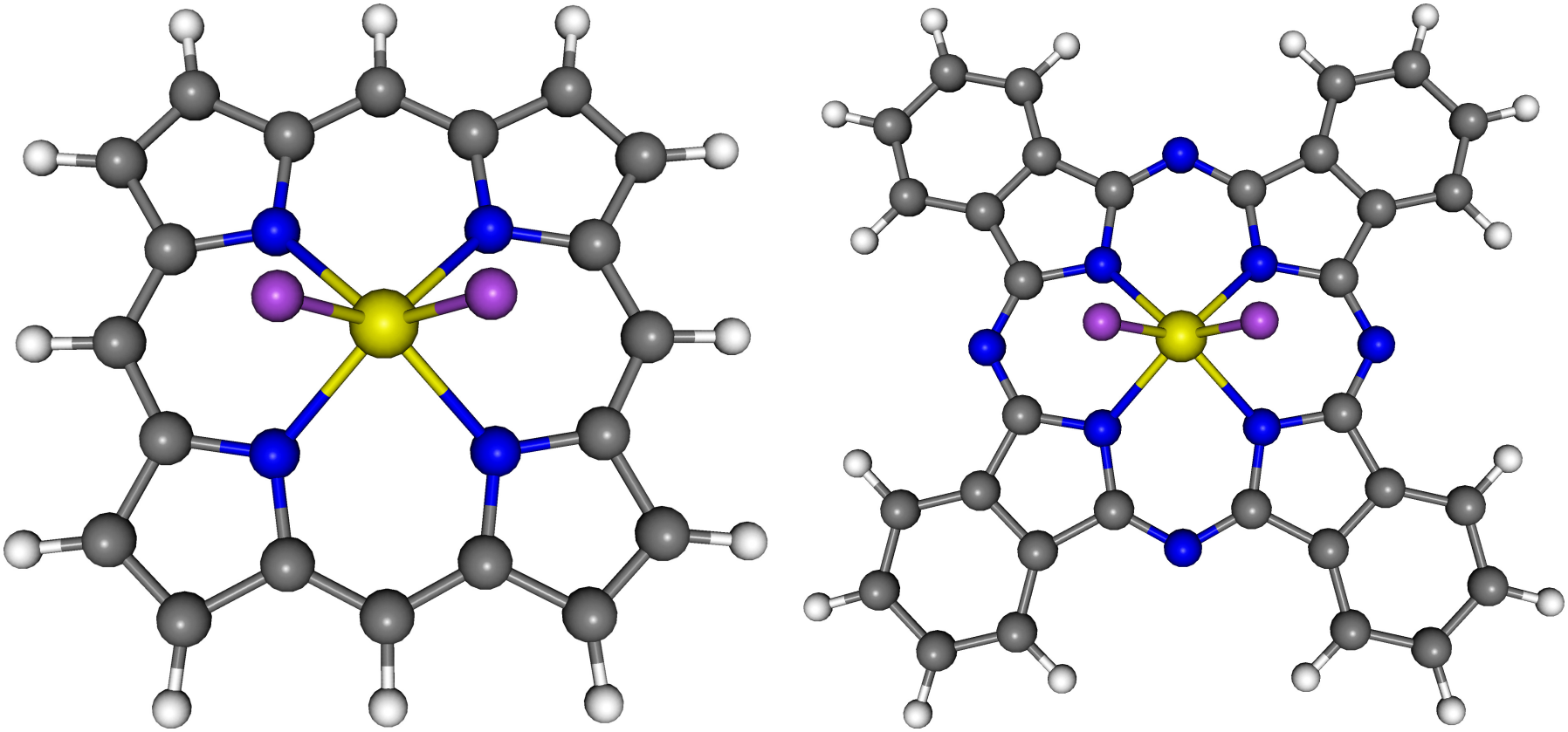
Experimental (dots) and theoretical (full line) radial distribution curves for TiOPc and difference curve (below).

Structural parameters of oxotitanium phthalocyanine

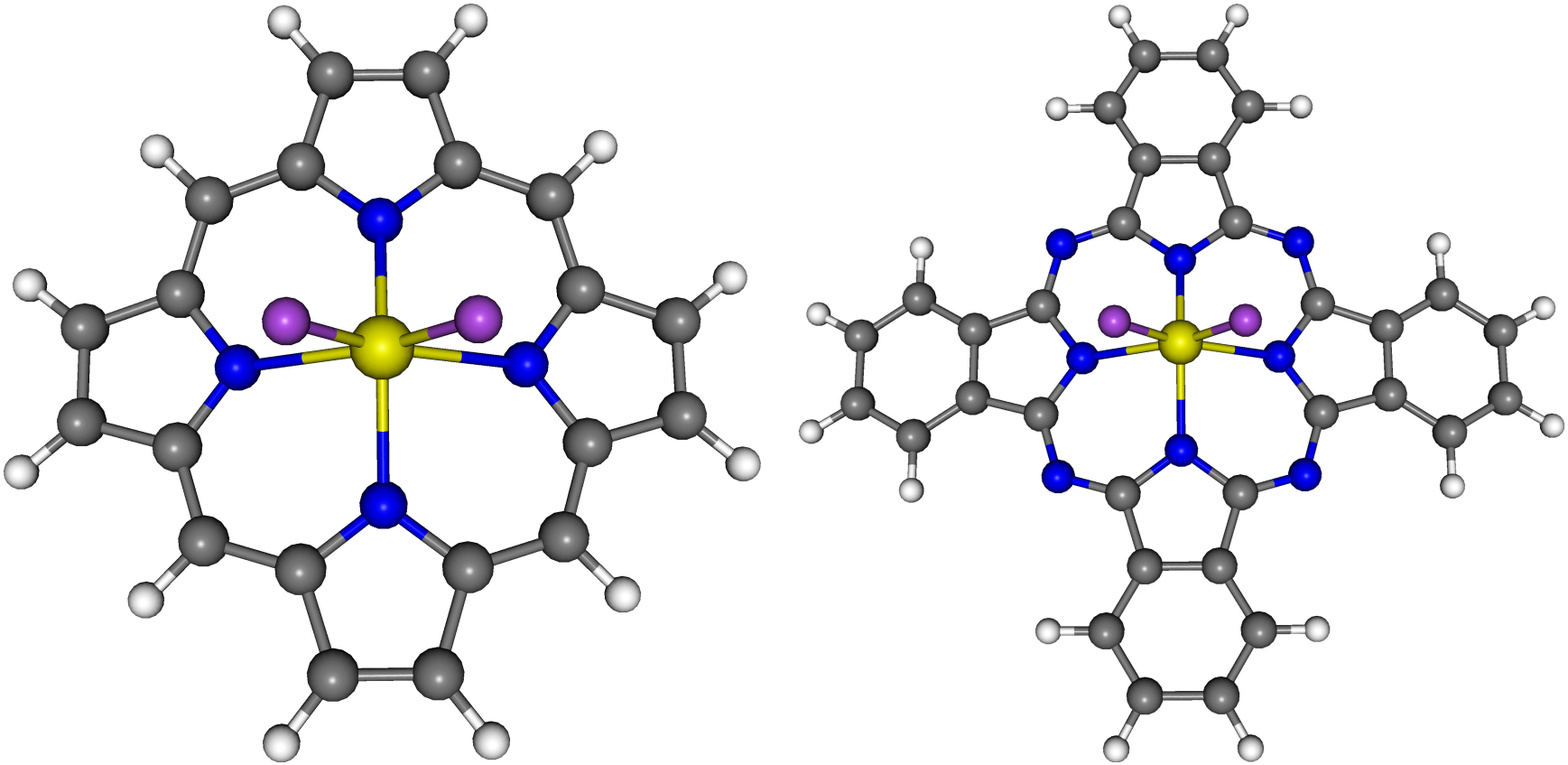
	Theoretical calculations			ED	X-ray [1]	
	1 [2]	2	3		α	β
Distances, Å						
r(Ti-O)	1.617	1.617	1.619	1.595(10)	1.650(4)	1.626(7)
r(Ti-N)	2.087	2.087	2.094	2.089(7)	2.066	2.066
r(N-C_{p1})	1.376	1.373	1.373	1.382(8)	1.376	1.378
r(N_m-C_{p1})	1.323	1.322	1.322	1.326(8)	1.330	1.326
r(C_{p1}-C_{p2})	1.456	1.454	1.454	1.449(9)	1.454	1.459
r(C_{p2}-C'_{p2})	1.406	1.404	1.404	1.400(21)	1.409	1.402
r(C_{p2}-C_{b1})	1.393	1.391	1.391	1.407(9)	1.383	1.387
r(C_{b1}-C_{b2})	1.391	1.388	1.388	1.405(9)	1.391	1.383
r(C_{b2}-C'_{b2})	1.406	1.403	1.403	1.388(24)	1.413	1.403
z(Ti)-z(N)	0.649	0.653	0.667	0.641	0.625	0.639
Valence and dihedral angles, degrees						
α(O-Ti-N)	108.1	108.2	108.6	107.9(8)	107.6	107.9
α(Ti-N-C_{p1})	124.6	124.6	124.6	124.3(7)		
α(N-C_{p1}-N_m)	127.5	127.4	127.5	126.4(8)		
γ(O-Ti-N-C_{p1})	81.9	81.9	81.9	80(3)		
γ(Ti-N-C_{p1}-N_m)	17.7	17.7	17.9	21(7)		



TiF_2P and TiF_2Pc, *trans* isomers (D_{4h} symmetry)



TiF_2P and TiF_2Pc, *cis* isomers (C_{2v} symmetry), halogens in the same plane with meso atoms



TiF_2P and TiF_2Pc, *cis* isomers (C_{2v} symmetry), halogens in the same plane with central nitrogen atoms

X-Ray crystallographic data

TiX_2TPP (X = F, Cl, Br; TPP - tetraphenylporphyrin) – *trans* isomers:

TiF_2TPP: J.-C. Marchon, J.-M. Latour, A. Grand, M. Belakhovsky, M. Loos, J. Goulon, *Inorg. Chem.*, 1990, **29**, 57;

$TiCl_2TPP$, $TiBr_2TPP$: A. N. Christensen, A. Grand, M. S. Lehmann, D. E. Cox, *Acta Chem. Scand.*, 1990, **44**, 103;

$TiBr_2TPP$: C. Lecomte, J. Protas, J.-C. Marchon, M. Nakajima, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **34**, 2856.

$TiCl_2Pc$ – *cis* isomer:

V. L. Goedken, G. Dessy, C. Ercolani, V. Fares, L. Gastaldi, *Inorg. Chem.*, 1985, **24**, 991.

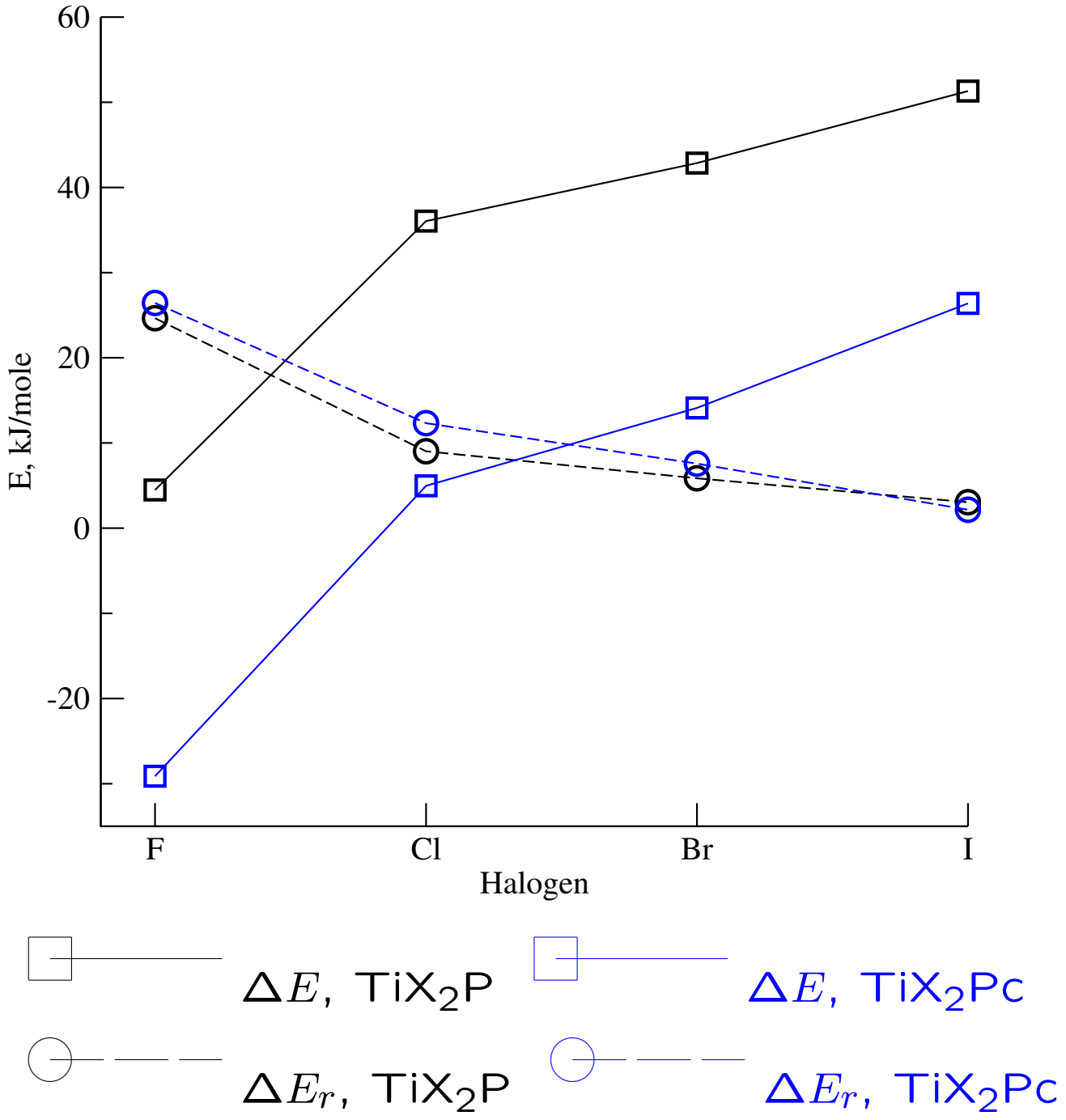
Computational

Ti: $8s7p6d1f/6s5p3d1f$ basis set and RECP (M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866)
C, N, H, F: $10s6p/5s3p$ basis set (T. H. Dunning, *J. Chem. Phys.*, 1971, **55**, 716) with one polarisation d function (C, N, F) or p function (H) and one diffuse p function (F only)
Cl: $12s9p/6s5p$ basis set (A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639) with one polarisation d function and one diffuse p function
Br, I: $14s10p2d1f/3s3p2d1f$ (Br) or $14s10p3d1f/3s3p2d1f$ (I) basis sets and RECP (J. M. L. Martin, A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408) with one diffuse p function

Energy differences between *trans* isomers (D_{4h}) and *cis* isomers (C_{2v})

	ΔE, kJ/mol
TiF_2P	4.48
$TiCl_2P$	36.04
$TiBr_2P$	42.86
TiI_2P	51.31
TiF_2Pc	-29.13
$TiCl_2Pc$	4.97
$TiBr_2Pc$	14.11
TiI_2Pc	26.39

$\Delta E = E(C_{2v}) - E(D_{4h})$



Selected structural parameters of TiX_2P molecules

	F (D_{4h})	F (C_{2v})	Cl (D_{4h})	Cl (C_{2v})	Br (D_{4h})	I (D_{4h})
Distances, Å						
r(Ti-X)	1.813	1.799	2.315	2.327	2.483	2.746
r(Ti-N)	2.080	2.169	2.071	2.158	2.070	2.065
r(N-C_{p1})	1.370	1.376	1.372	1.378	1.373	1.375
r(C_m-C_{p1})	1.397	1.384	1.395	1.383	1.395	1.394
r(C_{p1}-C_{p2})	1.443	1.438	1.440	1.436	1.440	1.438
r(C_{p2}-C'_{p2})	1.363	1.359	1.364	1.359	1.364	1.364
r(C_m-H_m)	1.083	1.082	1.083	1.082	1.083	1.083
r(C_{p2}-H_p)	1.079	1.079	1.079	1.079	1.079	1.079
Valence angles, degrees						
α(Ti-N-C_{p1})	125.9	128.8	126.0	125.9	126.0	126.1
α(X-Ti-X)		85.0		82.9		

Selected structural parameters of TiX_2Pc molecules

	F (D_{4h})	F (C_{2v})	Cl (D_{4h})	Cl (C_{2v})	Br (D_{4h})	I (D_{4h})
Distances, Å						
r(Ti-X)	1.820	1.800	2.325	2.319	2.492	2.751
r(Ti-N)	2.029	2.125	2.021	2.119	2.019	2.015
r(N-C_{p1})	1.372	1.377	1.375	1.380	1.376	1.378
r(C_m-C_{p1})	1.328	1.319	1.326	1.317	1.326	1.325
r(C_{p1}-C_{p2})	1.459	1.452	1.457	1.450	1.456	1.455
r(C_{p2}-C'_{p2})	1.412	1.402	1.411	1.401	1.412	1.412
r(C_{p2}-C_{b1})	1.392	1.394	1.393	1.394	1.393	1.393
r(C_{b1}-C_{b2})	1.391	1.390	1.391	1.389	1.391	1.390
r(C_{b2}-C'_{b2})	1.405	1.407	1.405	1.407	1.405	1.406
r(C_{b1}-H_{b1})	1.082	1.082	1.082	1.082	1.082	1.082
r(C_{b2}-H_{b2})	1.083	1.083	1.083	1.083	1.083	1.083
Valence angles, degrees						
α(Ti-N-C_{p1})	124.4	127.3	124.6	125.8	124.6	124.7
α(X-Ti-X)		85.9		83.7		