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ARTICLE TYPE

Phthalocyanine-titanate Nanotubes: a promising nanocarrier detectable by optical imaging in the so-called imaging window

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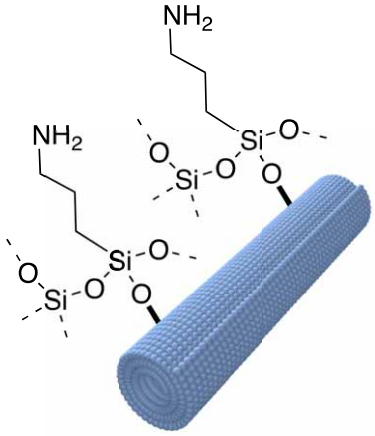
Outline

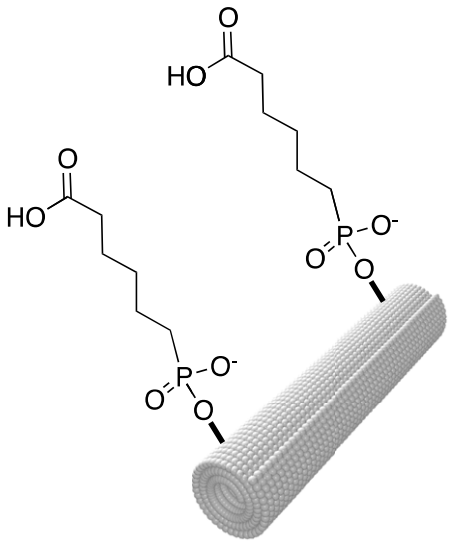
1. Drawings of Nanotubes (TiONts), Phthalocyanines (Pcs), and TiONt-Pcs Nanohybrids

Bare TiONts

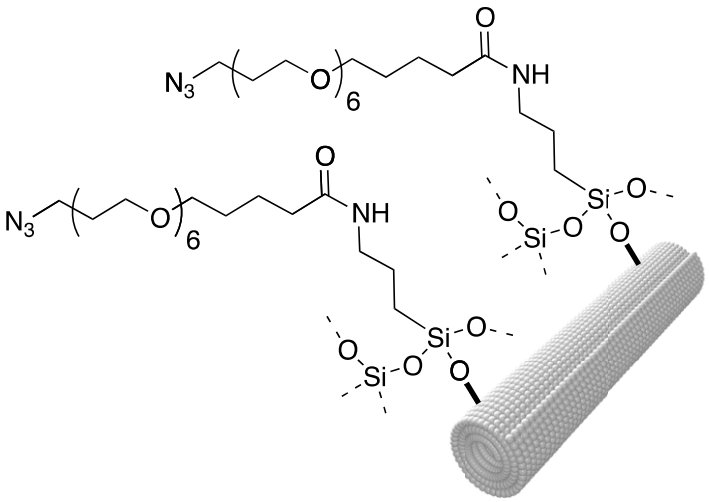
TiONts–NH_2 (2a)



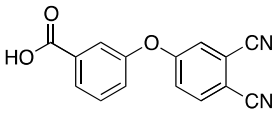
TiONts–COOH (2b)



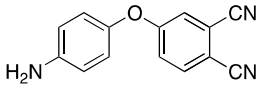
TiONts–N_3 (2c)



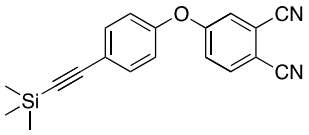
4-(carboxylato)phenoxy)phthalonitrile (4a)



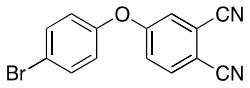
4-(amino)phenoxy)phthalonitrile (4b)



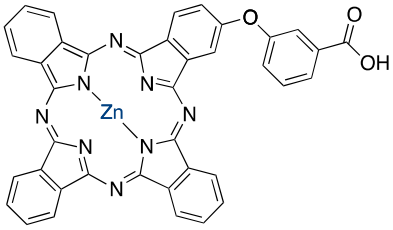
4-(4-((trimethylsilyl)ethynyl)phenoxy)phthalonitrile (4c)



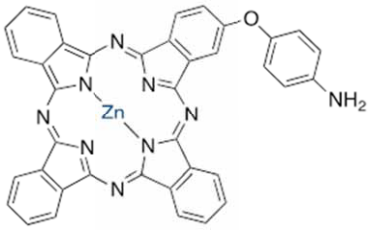
4-(4-bromophenoxy)phthalonitrile (4d)



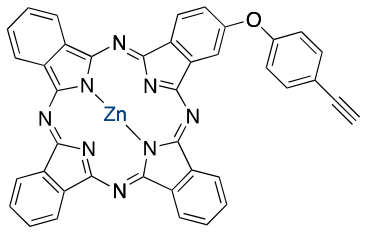
2-(4-(carboxy)phenoxy)-phthalocyaninato zinc(II) (3a)



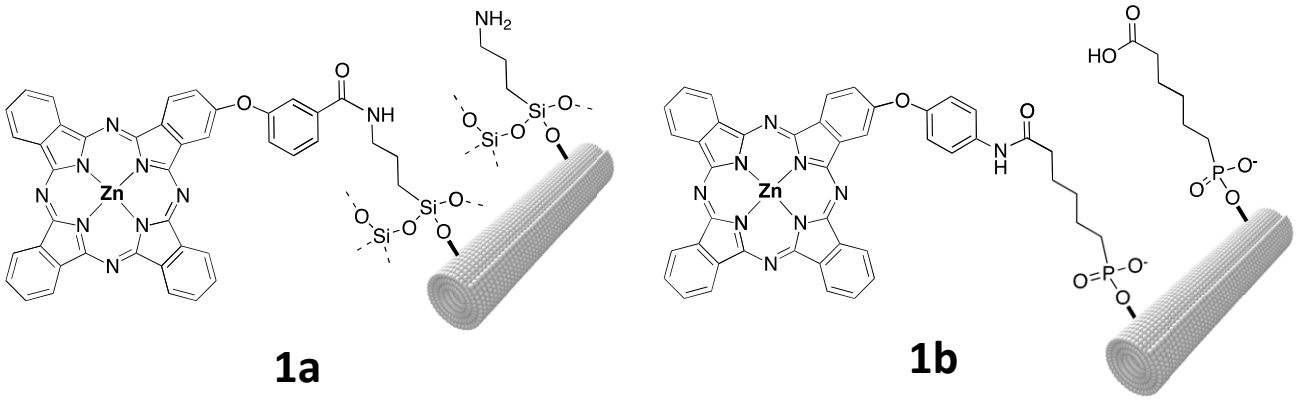
2-(4-(amino)phenoxy)-phthalocyaninato zinc(II) (3b)



2-(4-(alkynyl)phenoxy)-phthalocyaninato zinc(II) (3c)

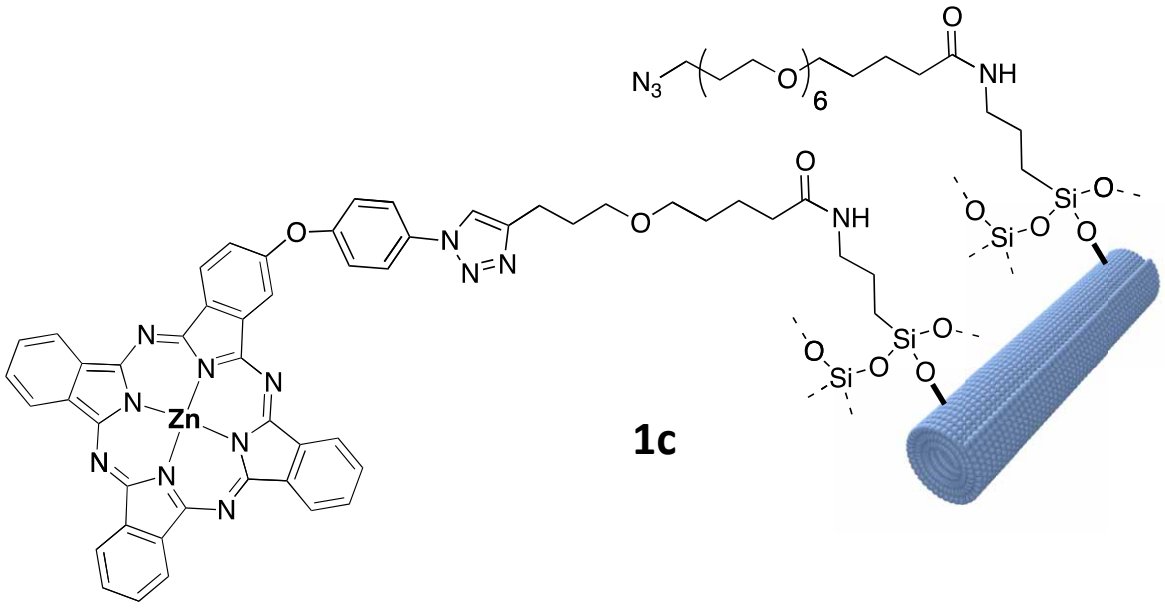


TiONts–Pc 1a/1b



1a 1b

TiONts–Pc 1c



1c

2. Characterizations of the bare nanotubes (TiONts) and functionalized–nanotubes (TiONts–X)

2.1. Characterization by TEM

2a

2b

2c

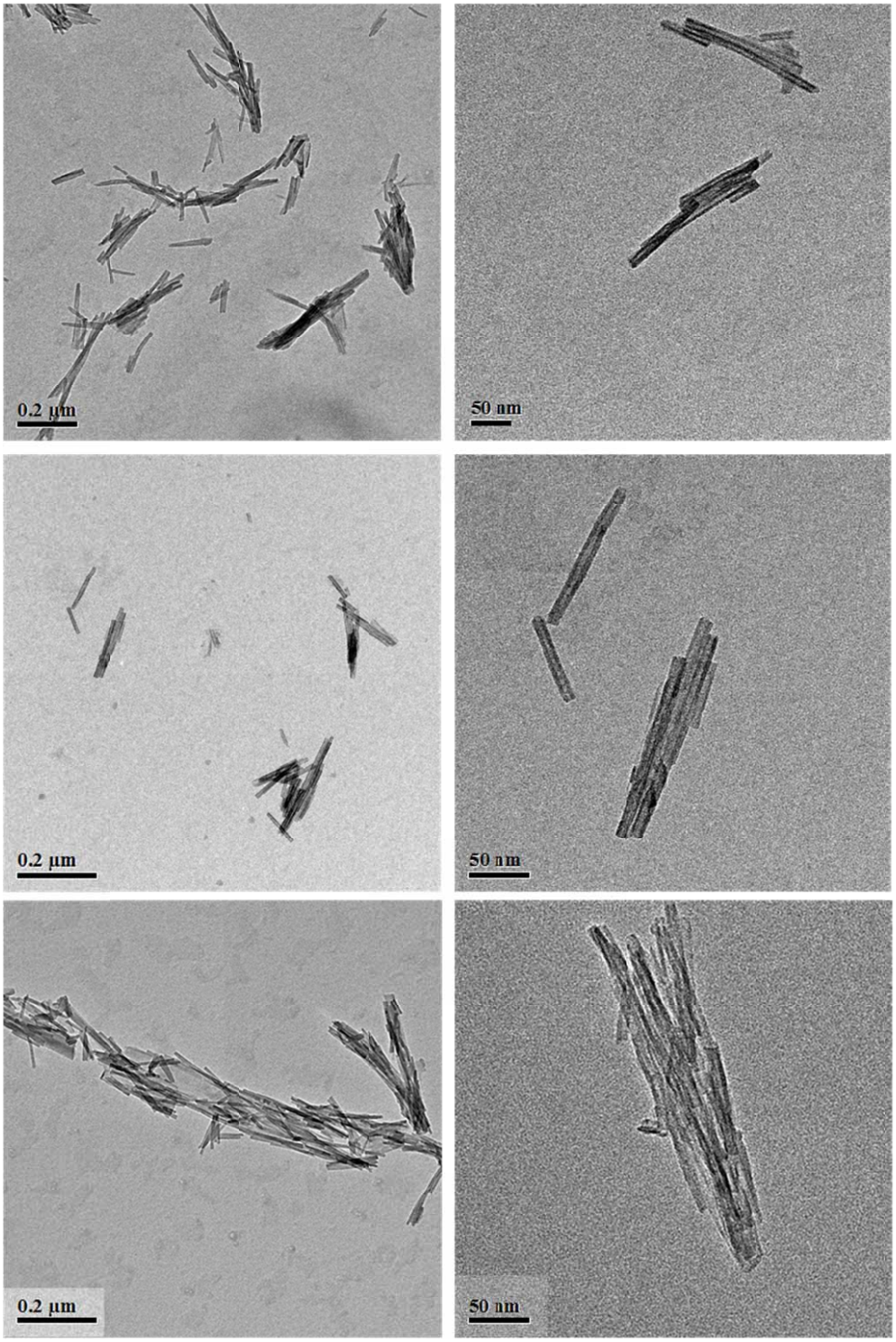


Fig S1bis. TEM images of functionalized titanate nanotubes (TiONts–X): 2a: TiONts–NH_2; 2b: TiONts–COOH; 2c: TiONts–N_3

2.2. Characterization by XPS

	Atomic concentration (%)						
	Ti 2p	O 1s	C 1s	Na KLL	N 1s	Si 2p	P 2p
TiONts	21	59	6	14	-	-	-
2a	19	54	13	8	3	3	-
2b	21	59	16	3	-	-	1
2c	16	49	23	4	6	2	-

Table S1. Atomic concentration of bare titanate nanotube and functionalized titanate nanotubes (TiONts–X): 2a: TiONts–NH_2; 2b: TiONts–COOH; 2c: TiONts–N_3

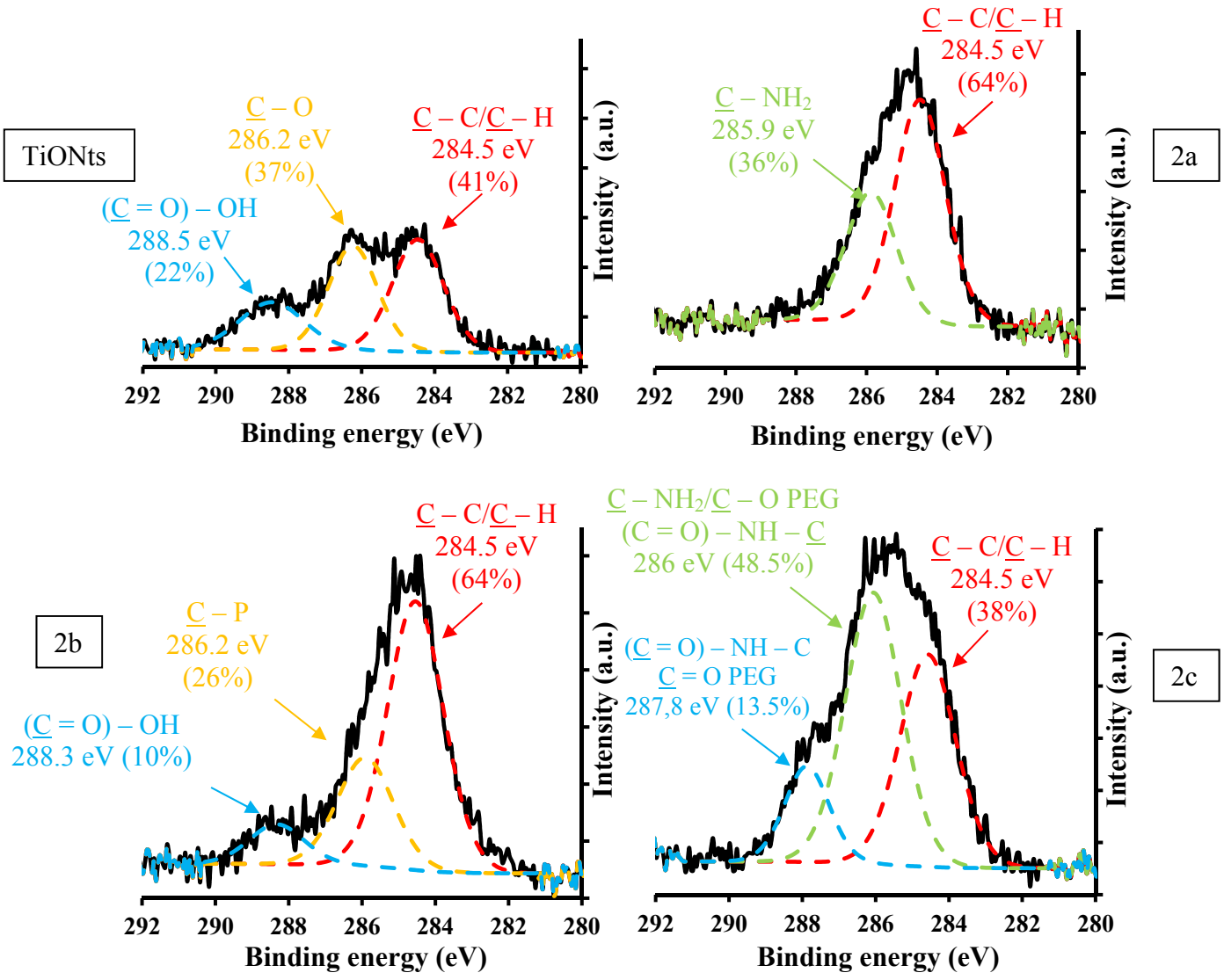


Fig S2. C1s contribution of bare titanate nanotubes and functionalized titanate nanotubes (TiONts–X): 2a: TiONts–NH_2; 2b: TiONts–COOH; 2c: TiONts–N_3

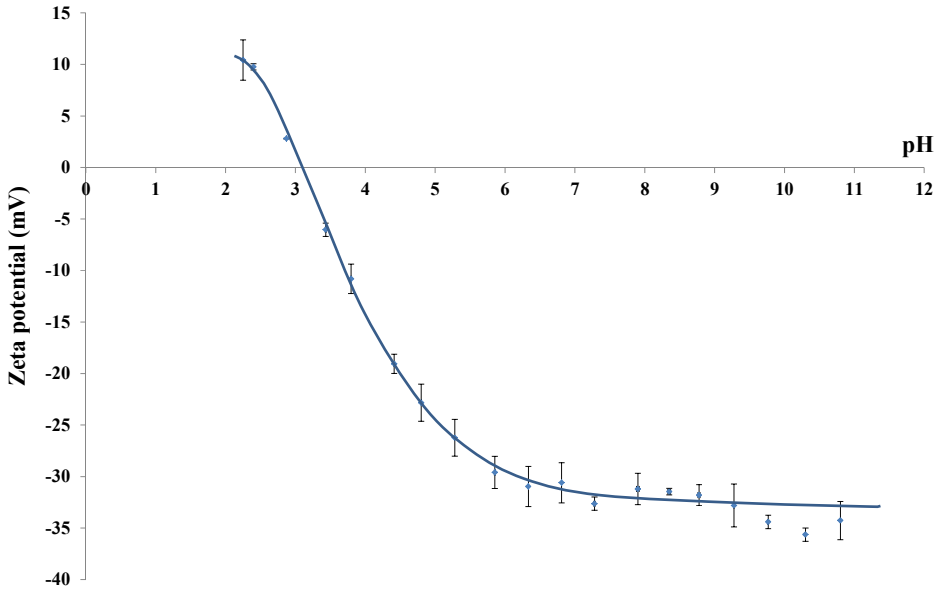


Fig S2bis. Zeta-potential of functionalized nanotubes TiONts-COOH 2b

3. 1H-NMR Characterization of the A3B+A4 phthalocyanine mixture

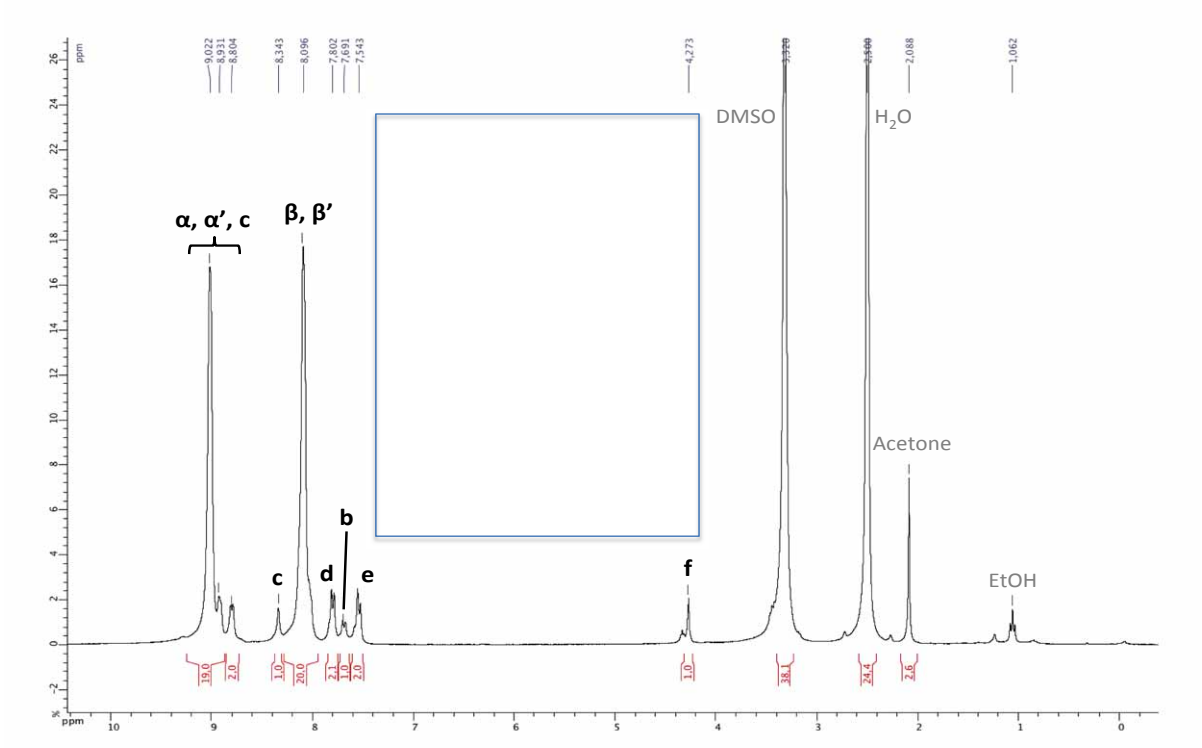


Fig. 2tris. 1H-NMR (300 MHz, in DMSO-d6, 300K) of the A3B+A4 phthalocyanine mixture (Ratio A3B:A4 is 4:7).

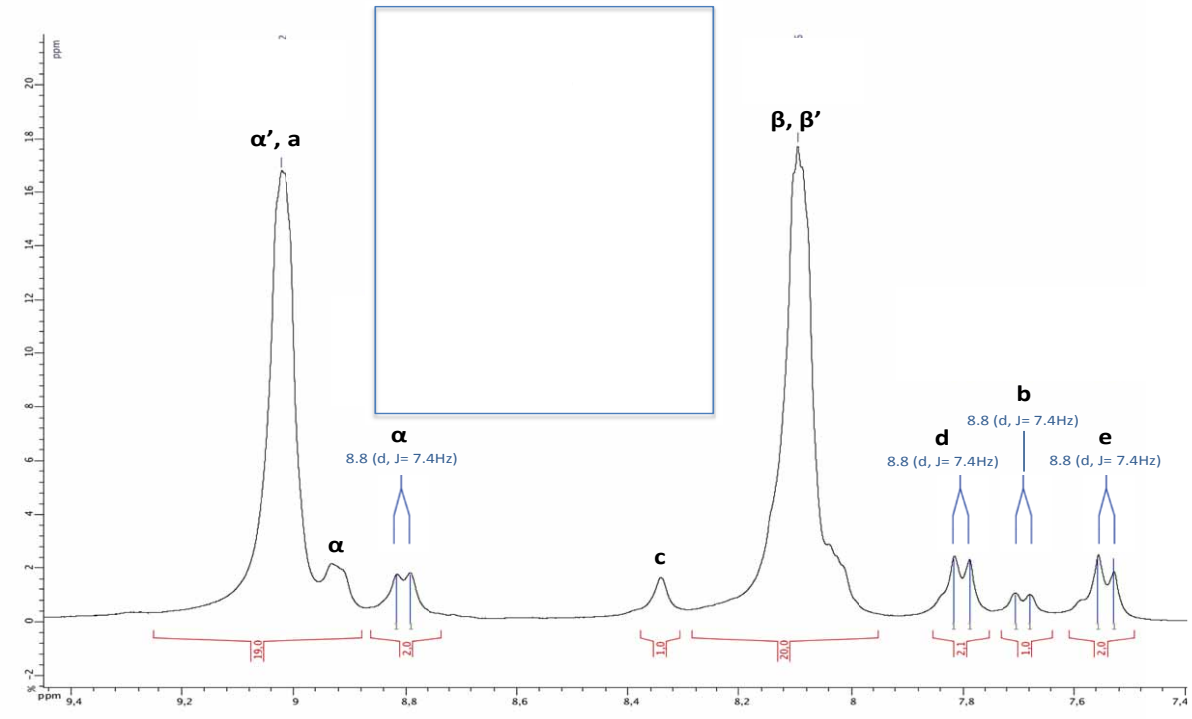


Fig S2tris. 1H-NMR of the A3B+A4 phthalocyanine mixture. (Continued)

4. Characterizations of the TiONts–Pc conjugates 1a and 1b

4.1. Characterization by TEM

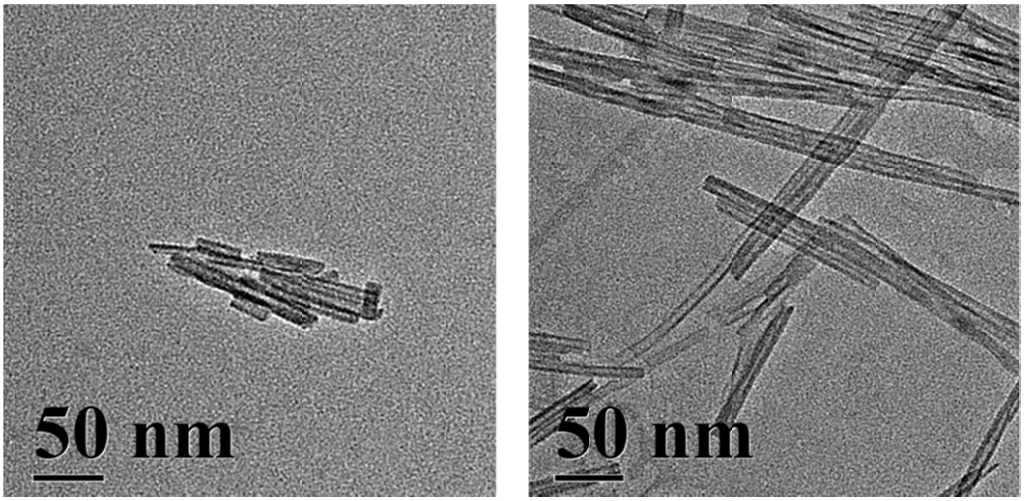


Fig S3. TEM micrographs showing (A) TiONts–Pc **1a**, (B) TiONts–Pc **1b** (note that the concentration in this sample was high enough to demonstrate this peculiar organization, this is not due to agglomeration)

4.2. Characterization by XPS

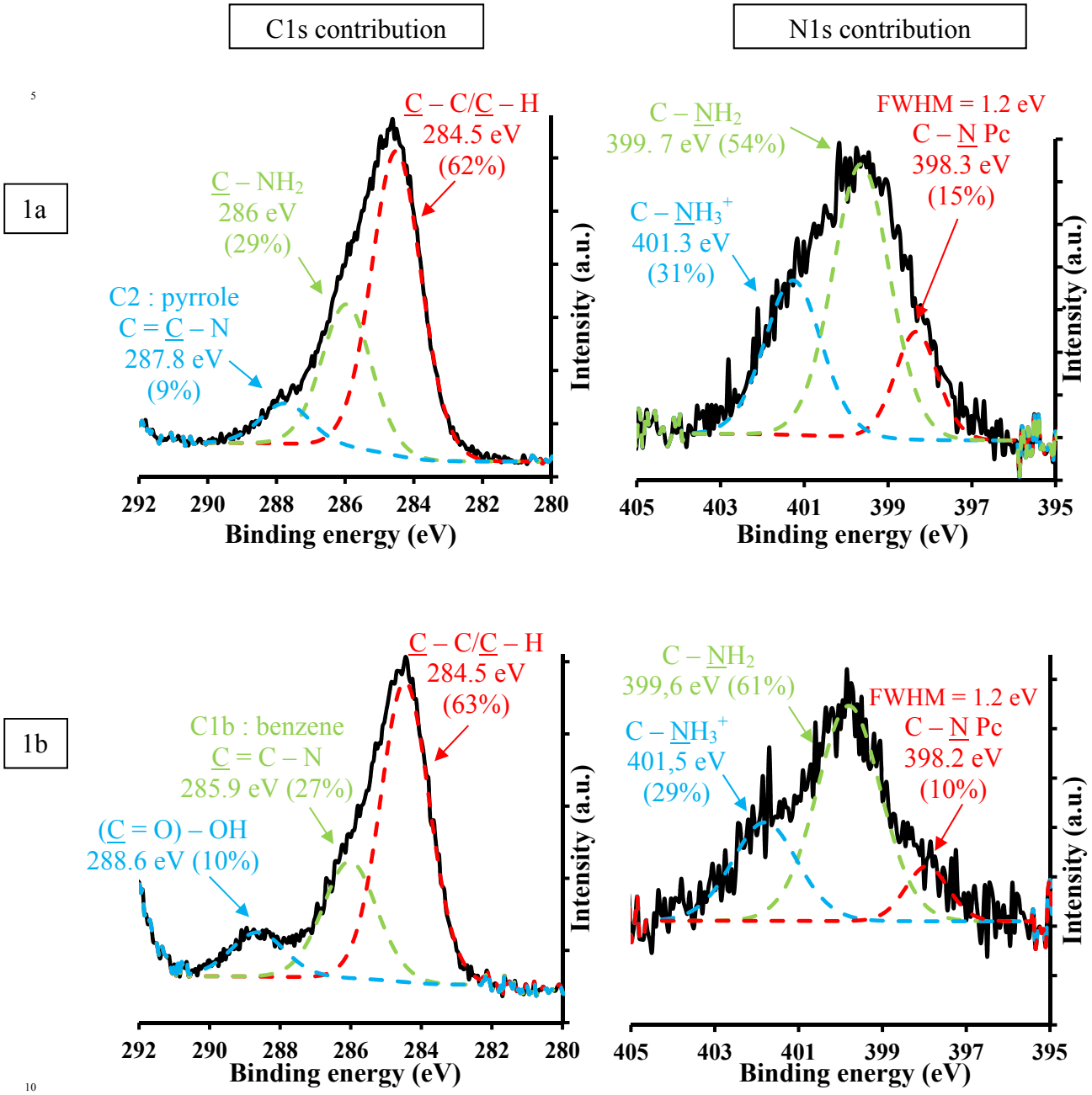


Fig S4. XPS spectra for C1s and N1s contribution in conjugate TiONts–Pc 1a and 1b

4.3. Characterization by TGA

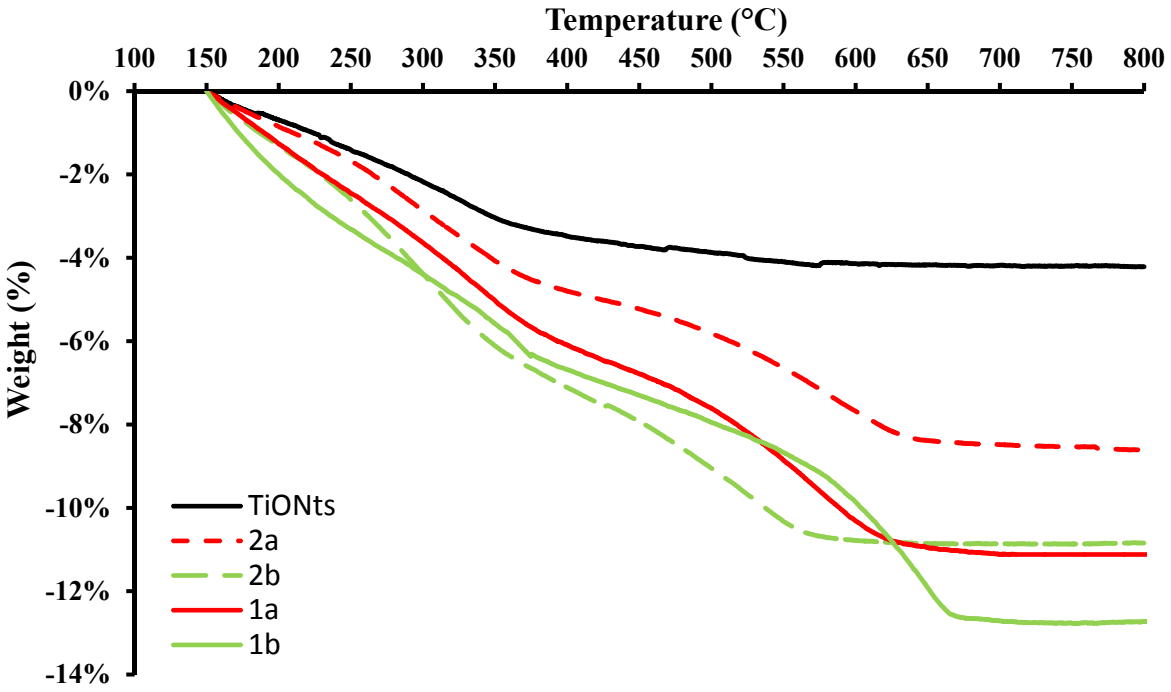


Fig S5. TGA curves of bare titanate nanotube (TiONts), functionalized titanate nanotubes (TiONts–X): 2a: TiONts–NH_2; 2b: TiONts–COOH and conjugate TiONts–Pc 1a-b

	Total Δm (%)	calc. Δm (%)	Molar mass M_{XX} (g.mol^{-1})	molecules/nm^2
TiONts	3.8	3.8	18	6.0 OH
2a	8.0	8.0	58	5.7 NH_2
1a	11.1	3.1	714	0.15 Pc
2b	10.9	10.9	115	3.1 COOH
1b	12. 8	1.9	685	0.1 Pc

Table S2. TGA results of bare titanate nanotube (TiONts), functionalized titanate nanotubes (TiONts–X): 2a: TiONts–NH_2; 2b: TiONts–COOH; 2c: TiONts–N_3 and conjugate TiONts–Pc 1a, 1b and 1c

The coverage is calculated as follows:

$$N_{Molecules} = \frac{(\text{calc. } \Delta\text{m}).N_A}{M_{XX}.S_{BET}.10^{18}}$$

Area calculations of TiONts (cylinder area): $A = 2\pi rh$

The outer surface of a cylinder 156 nm long (h) , 9.1 nm in diameter (2r) is:
$A = 2\pi rh = 2\pi \times 9.1/2 \times 156 = 4460$ nm^2

Calculation of Pc/TiONts:

1a - TiONts-COOH/Pc = 0.15 Pc/nm^2 → 4460 × 0.15 = 669 Pc/TiONts

1b - TiONts-NH_2/Pc = 0.1 Pc/nm^2 → 4460 × 0.1 = 446 Pc/TiONts

1c - TiONts-N_3/Pc = 0.1 Pc/nm^2 → 4460 × 0.1= 446 Pc/TiONts

4.4. Characterization by UV/Vis

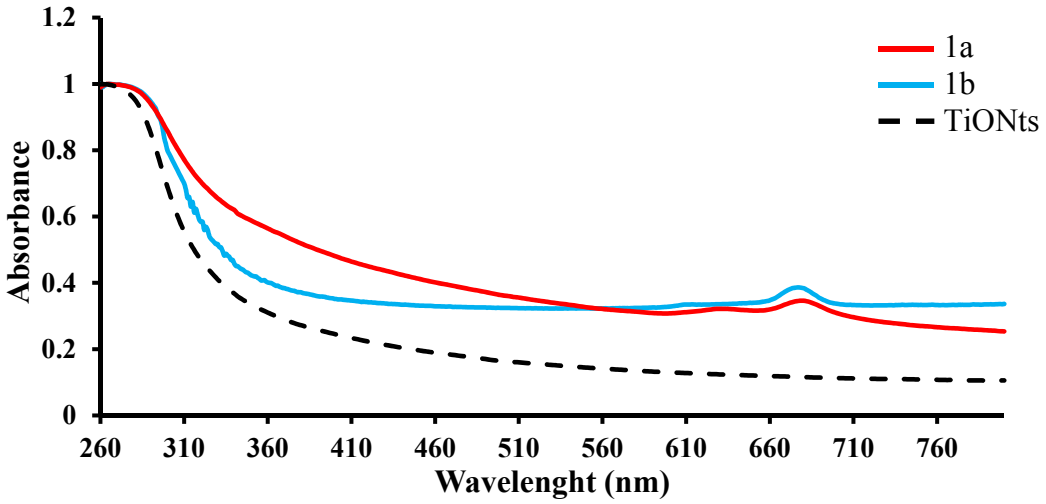


Fig S6. UV/Vis spectra in DMSO of conjugate TiONts–Pc 1a and 1b, compared to that of bare titanate nanotubes (TiONts).

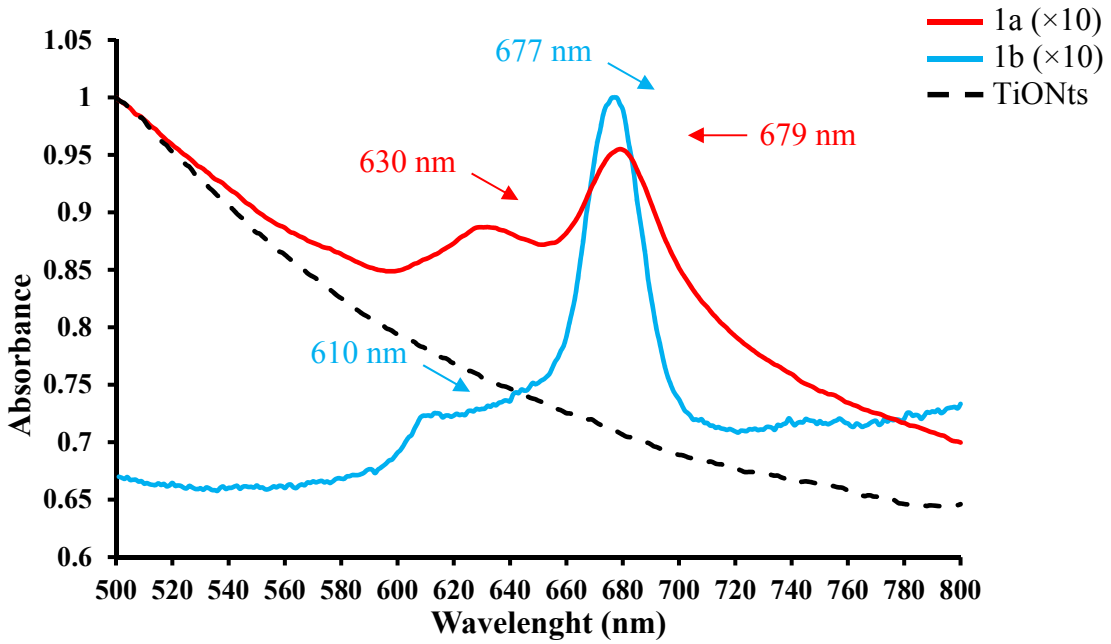


Fig S7. Magnification of the UV/Vis spectrum in DMSO of conjugate TiONts–Pc 1a and 1b in the 500–800 region exhibiting the Q bands characteristic of phthalocyanines.

4.5. Fluorescence Imaging Properties of TiONts–Pc Conjugates 1a-b

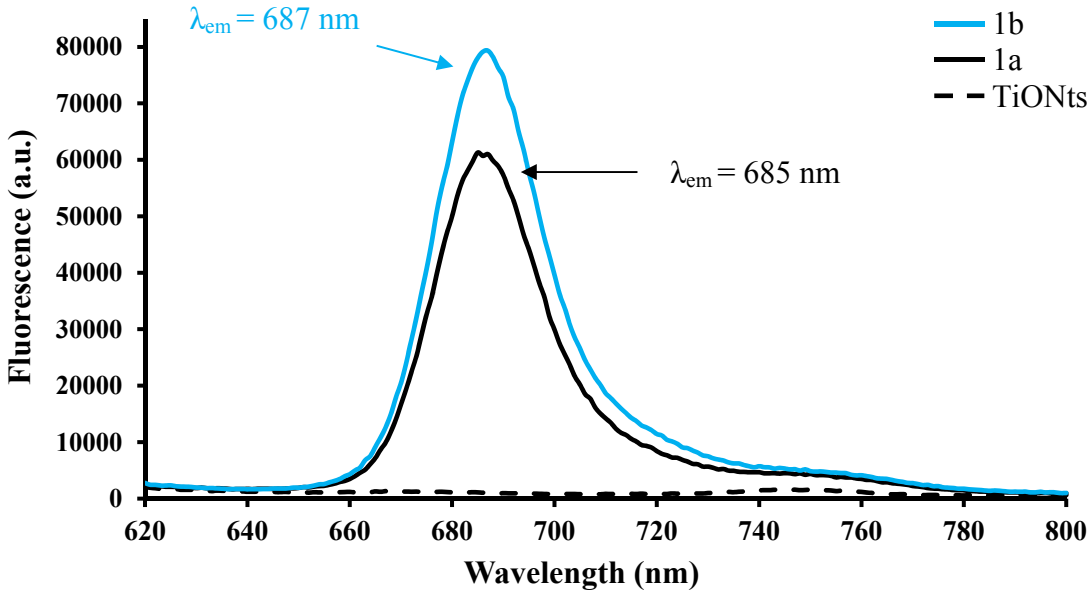


Fig S8. Fluorescence spectra of conjugates 1a and 1b, compared to that of bare titanate nanotubes (TiONts) in DMSO.

5. Characterizations of the TiONts–Pc conjugates 1c

5.1. Characterization by XPS

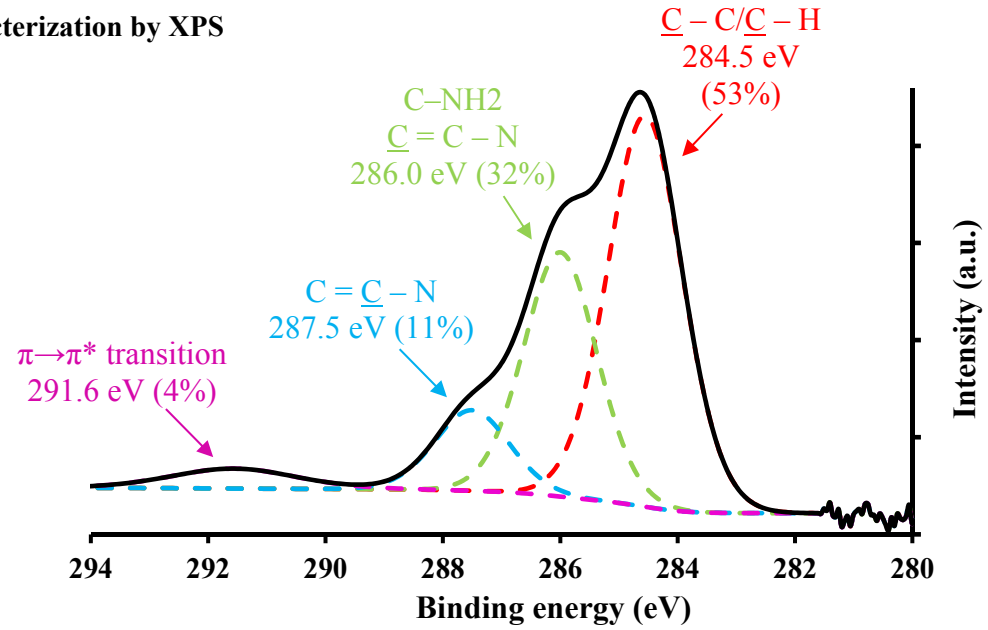


Fig S9. XPS spectra for C1s contribution in conjugate TiONts–Pc 1c

5.2. Characterization by TGA

	Total Δm (%)	calc. Δm (%)	Molar mass M_{XX} (g.mol^{-1})	molecules/nm^2
2c	19.3	9.2	555	0.6 PEG-N_3
1c	21.1	1.8	692	0.1 ZnPc

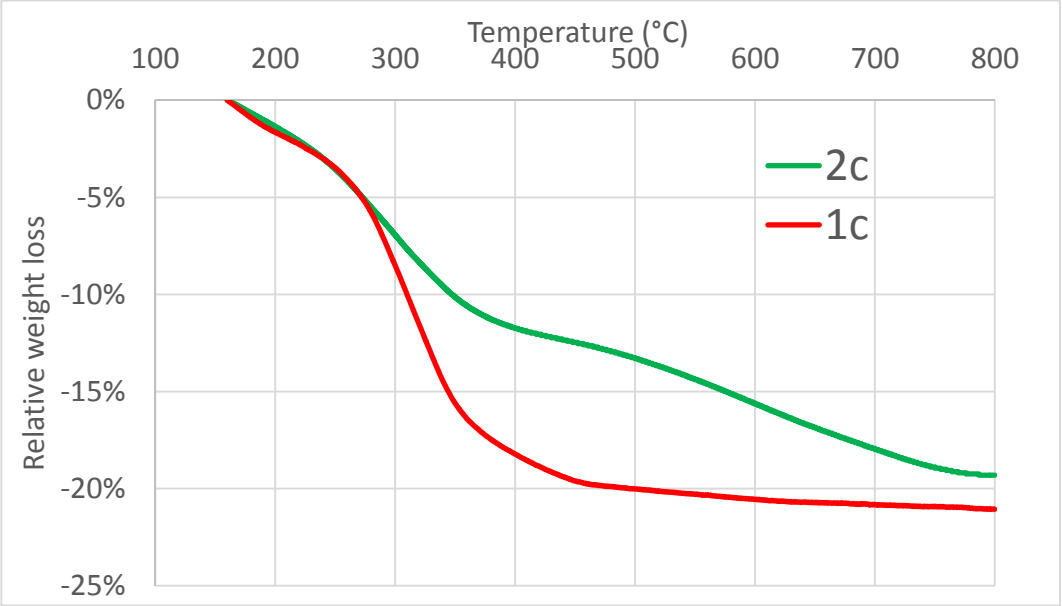


Fig S10. TGA curves of functionalized titanate nanotubes (TiONts–X): **2c**: TiONts–N_3 and conjugate TiONts–Pc **1c**

Fig S11. Conjugates a) TiONts–Pc **1a**, b) TiONts–Pc **1b** c) TiONts–Pc **1c** (as prepared suspension for zeta-potential measurement)