Novel Fluorous Amphiphilic Heteroleptic Ru-based Complexes for Dye-sensitized Solar Cell: The First Fluorous Bis-ponytailed Amphiphilic Ru Complexes

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Supporting Information (SI)

Materials. All reagents were obtained from commercial sources and used as received unless specified otherwise. Solvents were dried over sodium or CaH_2 before use. The fluorous ligands were synthesized as reported in the earlier publication. The structures of dyes **CT4, CT7** and **CT8** and their intermediates were identified with multi-nuclei NMR spectra. Samples analyzed by fast atom bombardment (FAB) mass spectroscopy were done by the staff of the National Central University (Taiwan) mass spectrometry laboratory. Infrared spectra were obtained on a Perkin–Elmer RX I FT-IR Spectrometer; and ATR data reported here were taken with ATR accessory (Pike Technology) with ZnSe crystal plate using typically 32 scans at a resolution of 4 cm^{-1}. UV/Vis spectra were recorded on SHIMADZU UV-360 spectrophotometer in a quartz cell with 1 cm path length. The emission spectra were recorded in the range of 550-800 nm on Fluoromax-4 spectrometer.

Synthesis of Ru[(dcbpy) (4,4'-bis($R_fCH_2OCH_2$)-2,2'-bpy)(NCS)2] (CT series dye)

Fig.s S1-S3: Drawings of CT7, CT8 and CT4 are shown in the following; (The multi-nuclei NMR spectra of CT 7 are also shown below.)

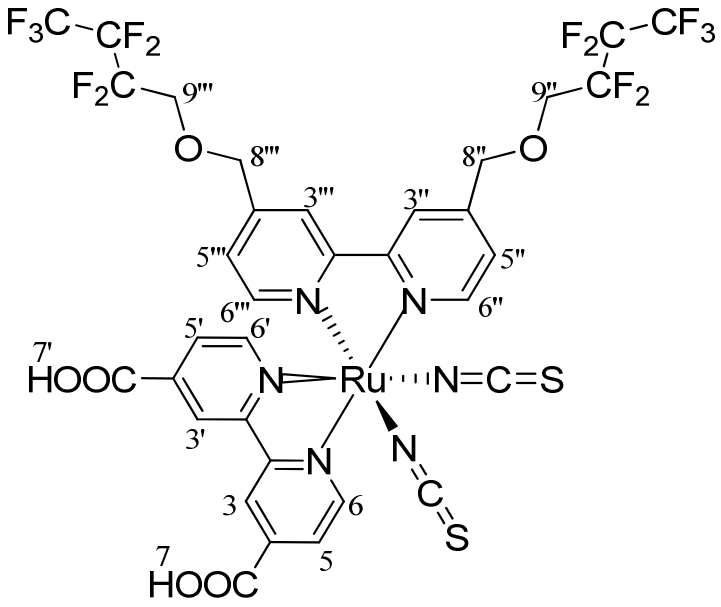

Fig. S1.1. Labeling for H atoms of CT7.

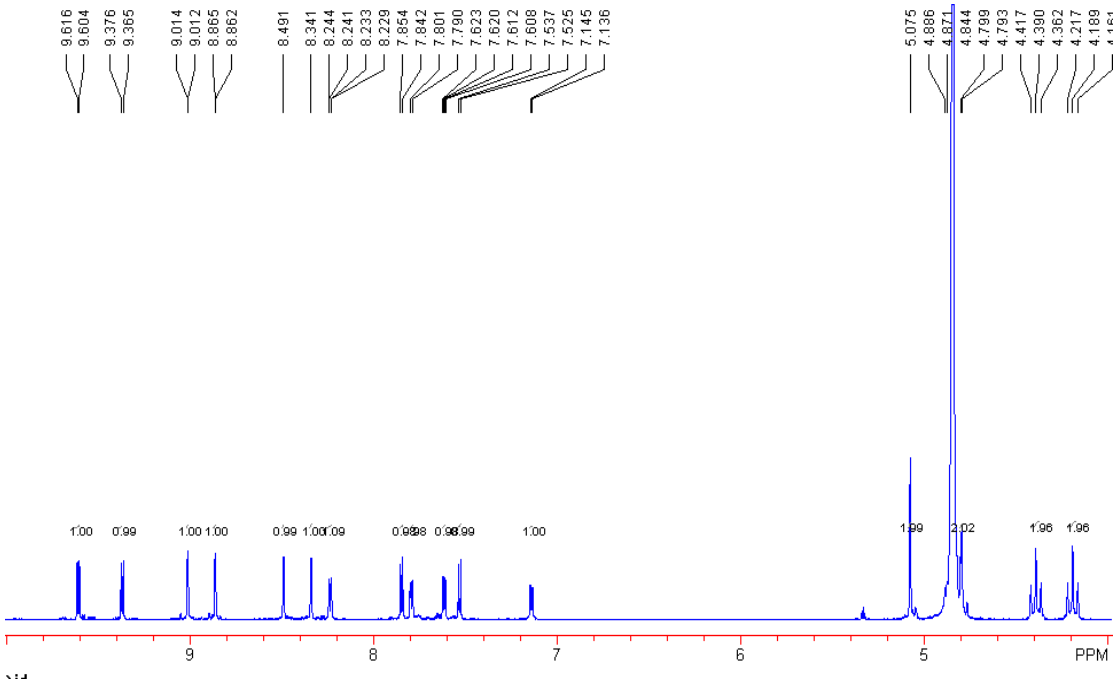

Fig. S1.1.1 ^{1}H NMR spectrum of CT7.

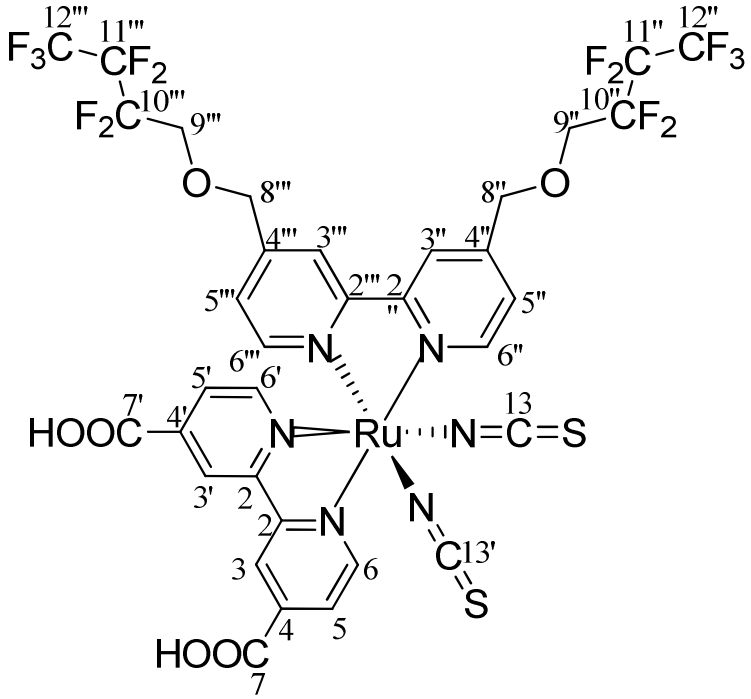

Fig. S1.2. Labeling for C atoms of CT7.

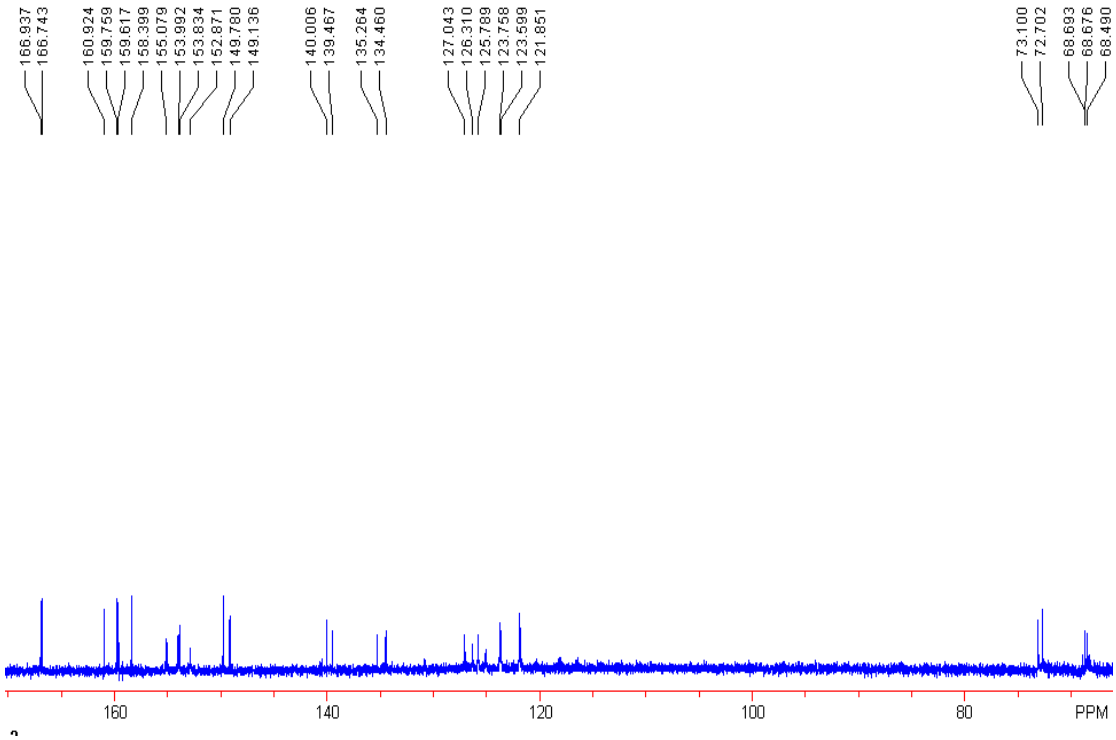

Fig. S1.2.1. ^{13}C NMR spectrum of CT7.

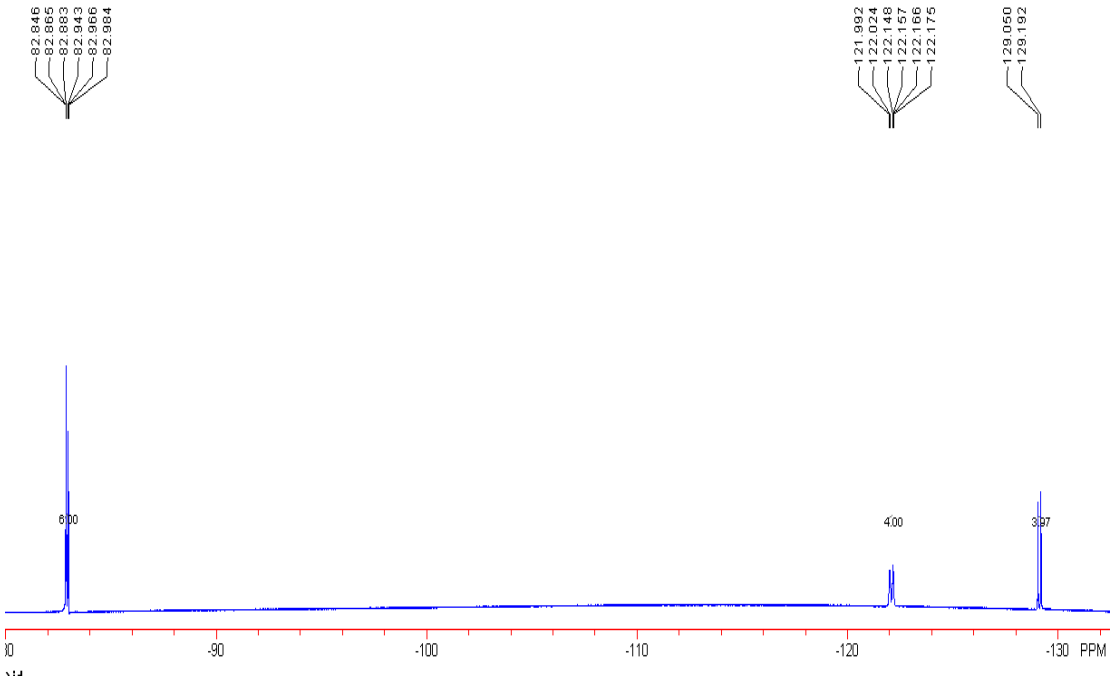

Fig. S1.3.1. ^{19}F NMR spectrum of CT7.

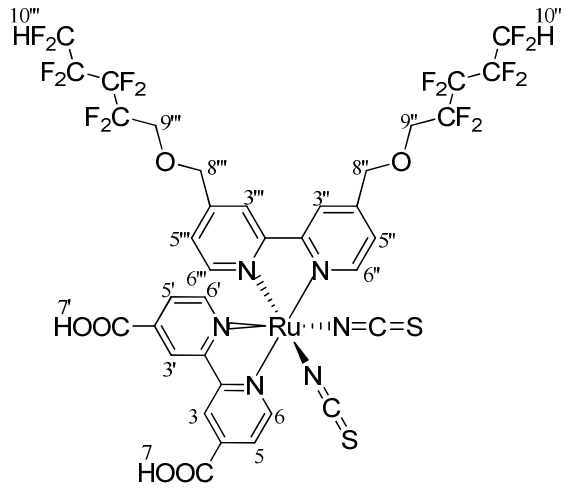

Fig. S2.1. Labeling for H atoms of CT8.

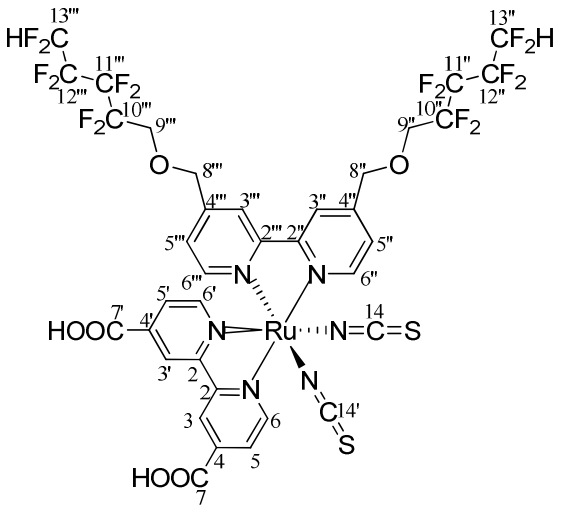

Fig. S2.2. Labeling for C atoms of CT8.

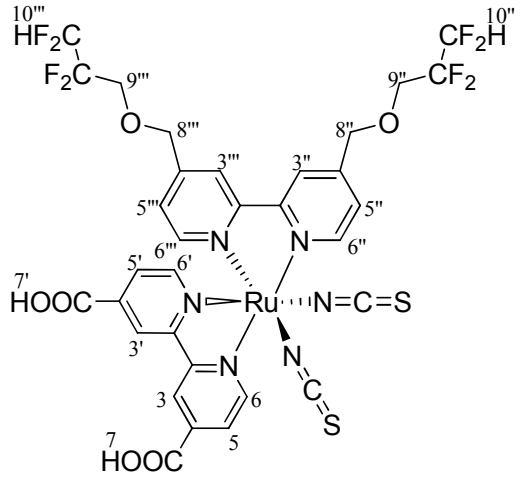

Fig. S3.1. Labeling for H atoms of CT4.

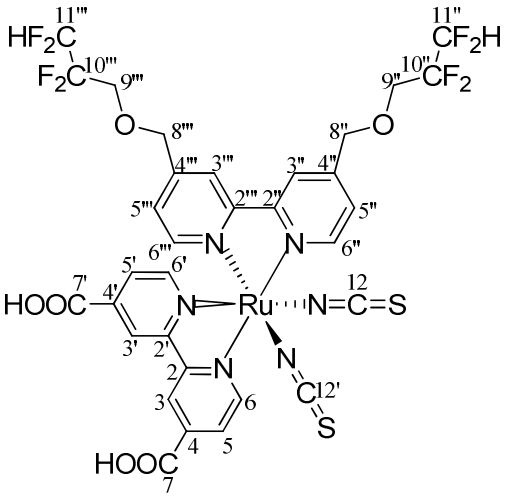

Fig. S3.2. Labeling for C atoms of CT4.

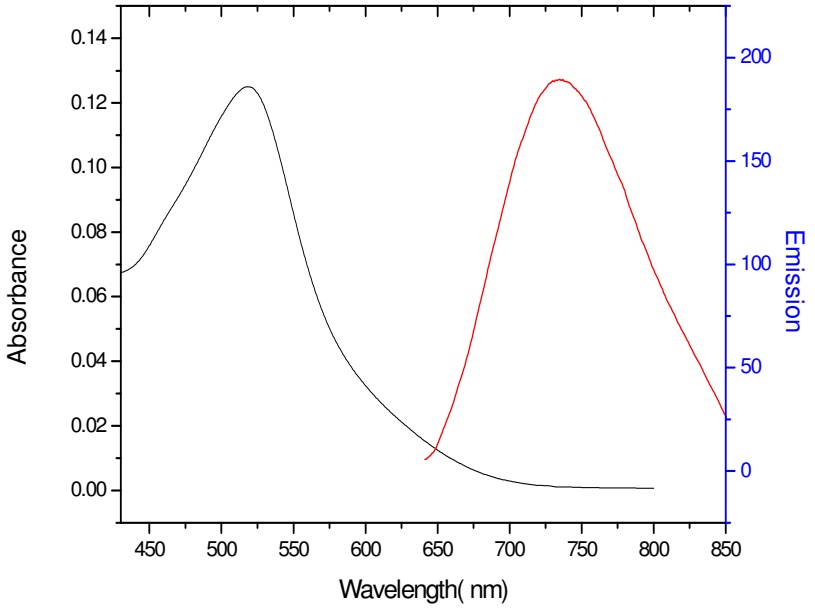

Fig. S4.1. The combined absorption and emission spectrum of CT4 (crossing-point at 648 nm).

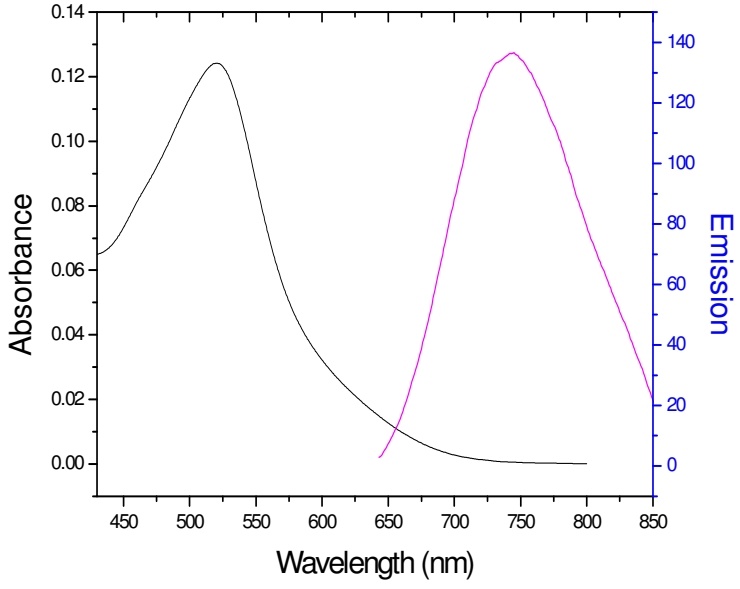

Fig. S4.2. The combined absorption and emission spectrum of CT7 (crossing-point at 654 nm).

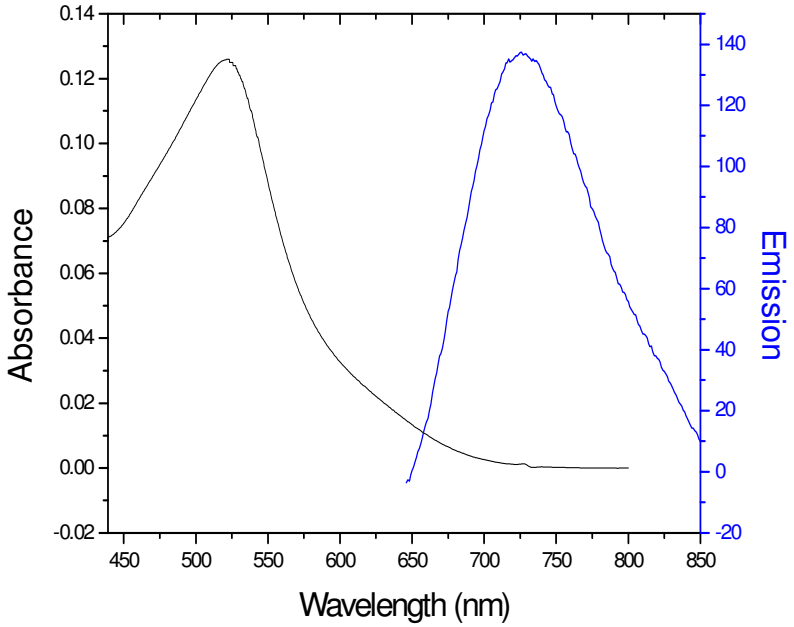

Fig. S4.3. The combined absorption and emission spectrum of CT8 (crossing-point at 658 nm).

IR spectral studies (IR spectra of the TBA salts of free CT7 and free CT8 and their respective adsorbed dyes are compared in a top and bottom manner); the salts of CT7 and CT8 used for the ATR-FTIR studies here are their TBA salts; their structures are:

[TBA.Ru(4,4'-bis($R_fCH_2OCH_2$)-2,2'-bipyridine)(4-carboxylicacid-4'-carboxylate-2,2'-bipyridine)$(NCS)_2$];

CT7 (R_f= C_3F_7), CT8 (R_f= HC_4F_8)}

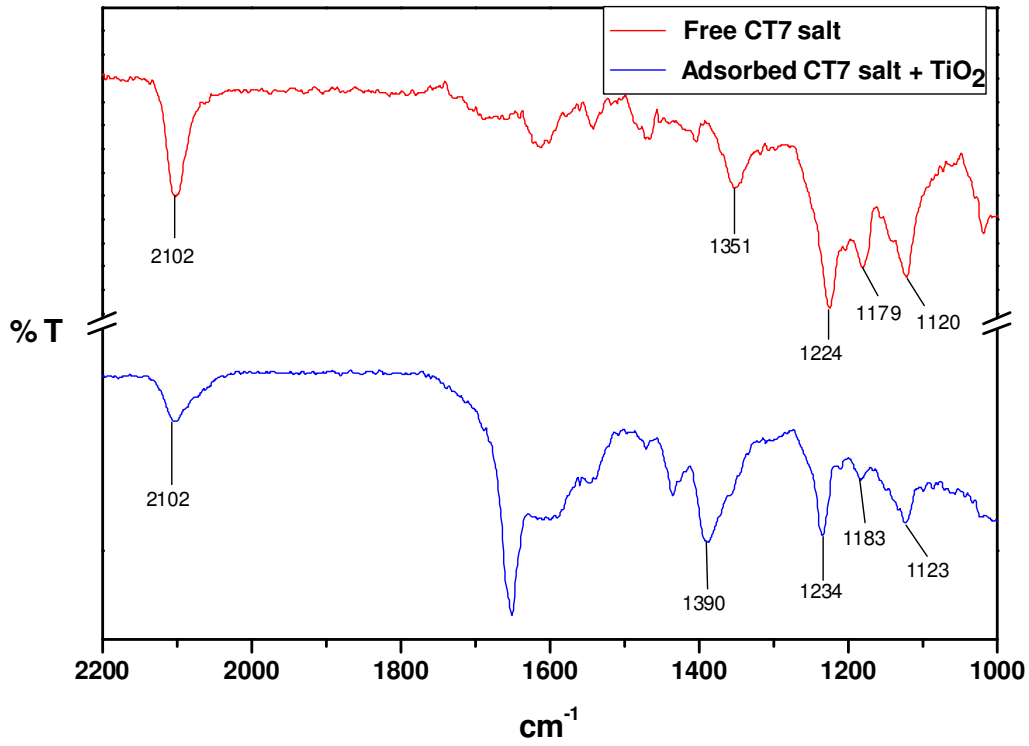

Fig. S5. ATR-FTIR spectra of the free (top) and the adsorbed (bottom) CT7 salts.

[CT7 salt: the asymmetric (ν_{as}) and symmetric (ν_s) stretching of CF_2 (or CF_3) groups were shifted from 1224 and 1120 cm^{-1} in the free dye to 1234 and 1123 cm^{-1} in the adsorbed CT7 salt, respectively.]

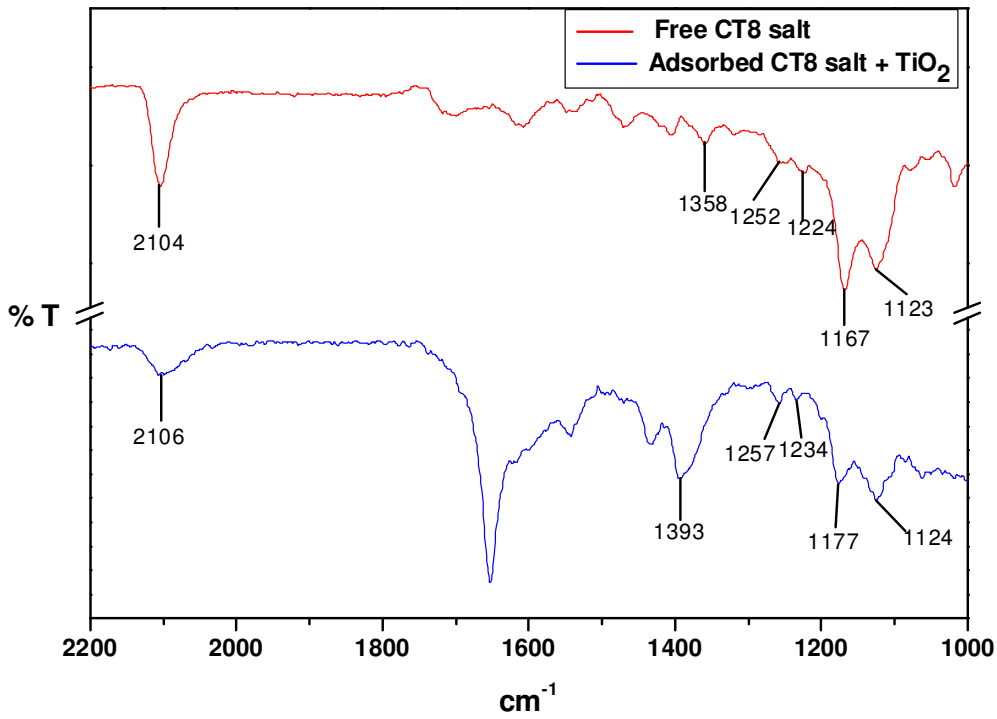

Fig. S6. ATR-FTIR spectra of the free (top) and the adsorbed (bottom) CT8 salts.
[CT8 salt: the asymmetric (ν_{as}) and symmetric (ν_s) stretching of CF_2 groups were shifted from 1167 and 1123 cm^{-1} in the free dye to 1177 and 1124 cm^{-1} in the adsorbed CT8 salt, respectively.]