Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Wavelength Dependent Nonlinear Optical Response of Tetraphenylethene Aggregation-induced emission luminogens

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Table S1. Crystal data and structure refinement for compounds **TPE**, **4Br-TPE** and **4I**-TPE

Compound No.	**TPE**	**4Br-TPE**	**4I-TPE**
Formula	$C_{26}H_{20}$	$C_{26}H_{16}Br_4$	$C_{26}H_{16}I_4$
Formula mass	332.42	648.03	835.99
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.8250(2)	9.6034(2)	9.8155(2)
b (Å)	9.4992(2)	15.4711(2)	15.6764(2)
c (Å)	10.7097(2)	22.0743(3)	22.6588(2)
α (°)	90.00	90.00	90.00
β (°)	107.106(2)	90.00	90.00
γ (°)	90.00	90.00	90.00
V (Å^3)	955.32(3)	3279.69(9)	3486.55(9)
Z	2	4	4
$D_{calcd.}$(g·cm^{-3})	1.156	1.312	1.593
μ (mm^{-1})	0.492	6.043	28.125
F (000)	352.0	1248	1536.0
θ (º)	4.32-74.14	3.49–73.42	4.82–73.19
GOF	1.063	1.134	1.077
R_1 (I>2sigma(I))	0.0519	0.0327	0.0585
wR_2 (all data)	0.1344	0.0937	0.1914

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

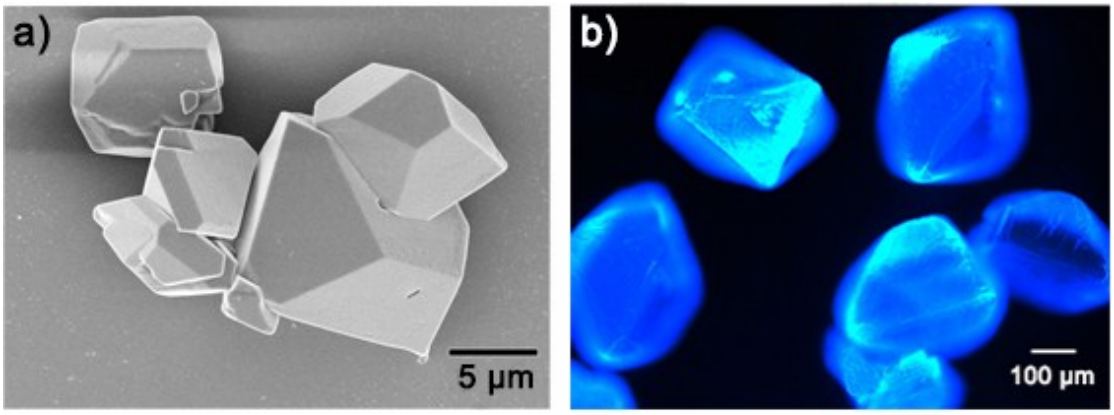

Fig. S1 Morphology (a) and fluorescent microscopy image (b) of TPE.

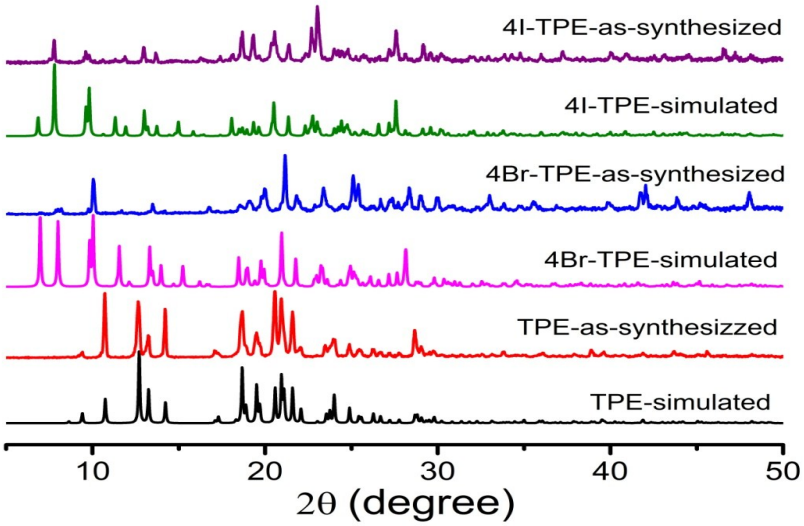

Fig. S2 The experimental and simulated PXRD patterns of compounds TPE, 4Br-TPE and 4I-TPE.

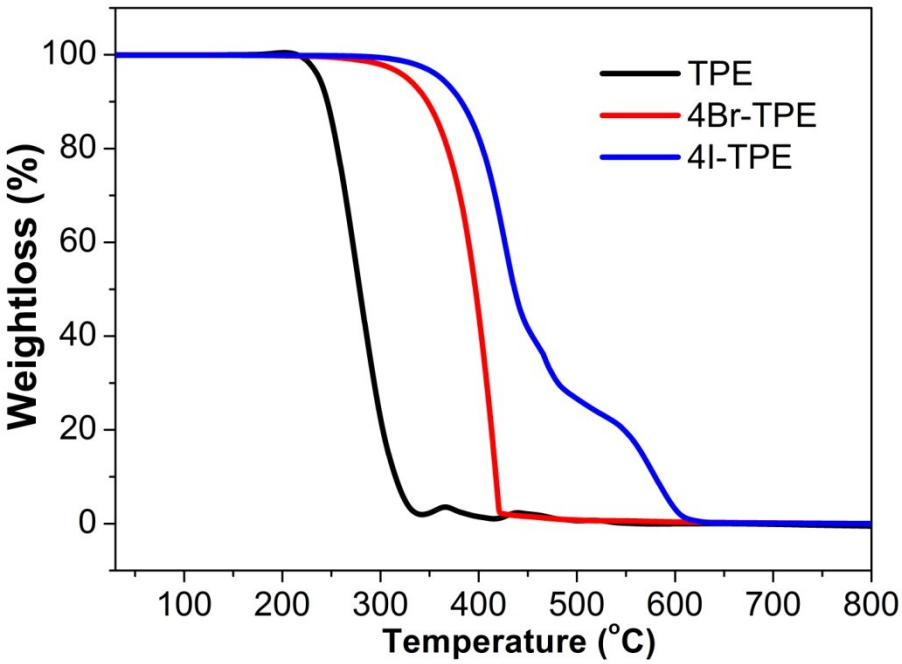

Fig. S3 TGA profiles of compounds TPE, 4Br-TPE and 4I-TPE.

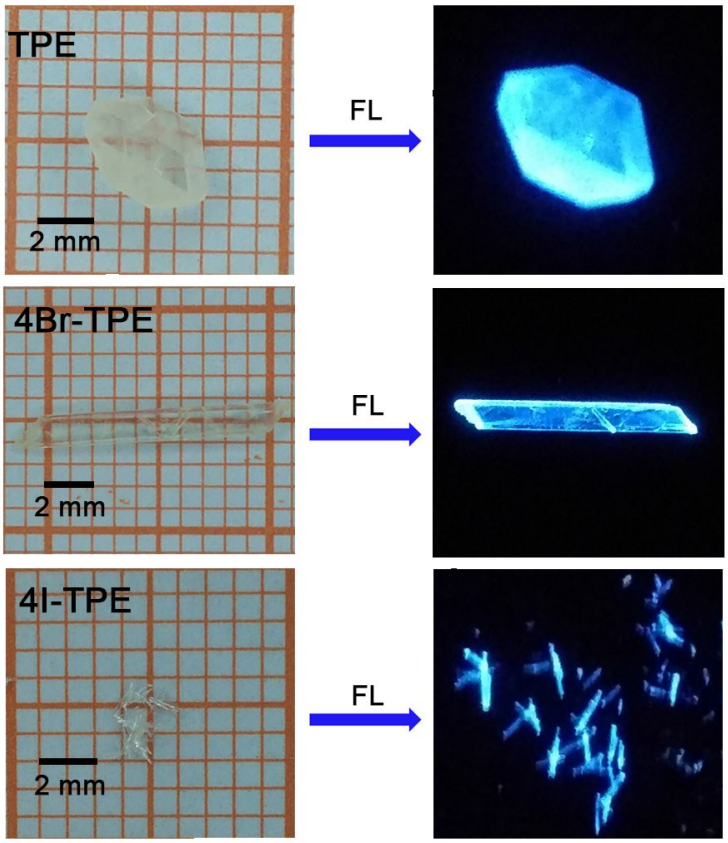

Fig. S4 Crystal morphology and fluorescence images of TPE, 4Br-TPE and 4I-TPE.

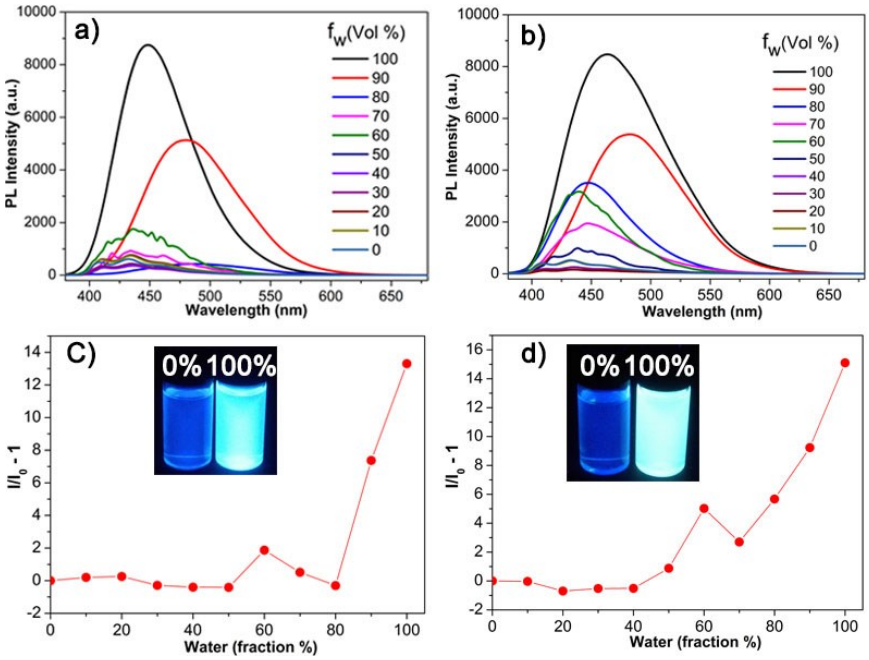

Fig. S5 Photoluminescence spectra of 4Br-TPE (a) and 4I-TPE (b) in H_2O/THF mixtures with water fractions (f_w) from 0 to 100% excited at 365 nm. Variations of the relative intensity (I/I_0 - 1) with f_w of 4Br-TPE (c) and 4I-TPE (d). The inset shows the photograph of the target compounds in THF (f w = 0, left) and in the H_2O (f_w = 100%, right) under 365 nm illumination, c = 0.2 mM.

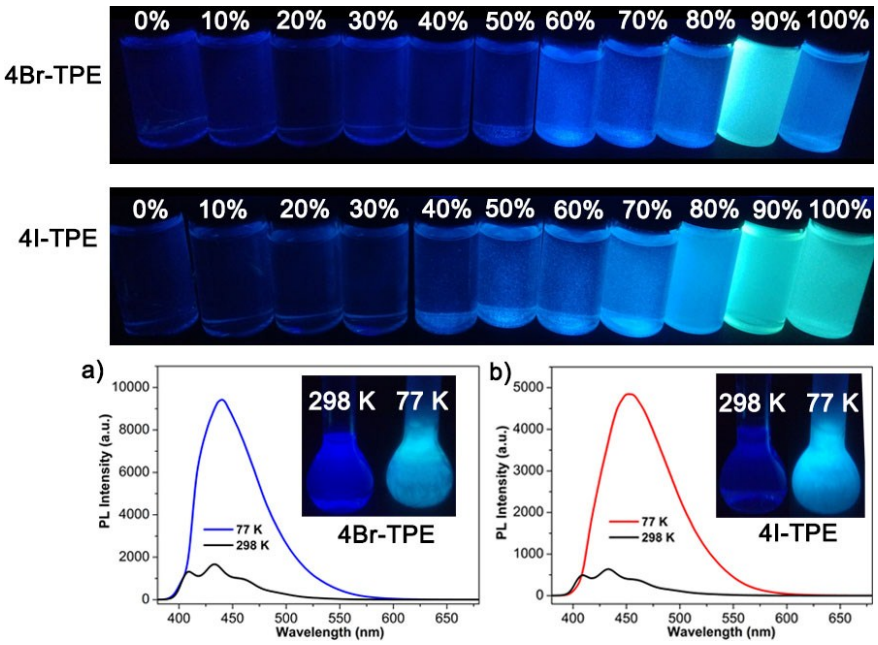

Fig. S6 Fluorescence images of 4Br-TPE and 4I-TPE in diverse H_2O/THF mixtures (0.2 mM) under a UV excitation (365 nm). Photoluminescence spectra of 4Br-TPE (a) and 4I-TPE (b) at 77 and 298 K in THF (excited at 365 nm). The inset shows the photograph of target compounds at 77 and 298 K in THF (under 365 nm illumination), c = 0.2 mM.

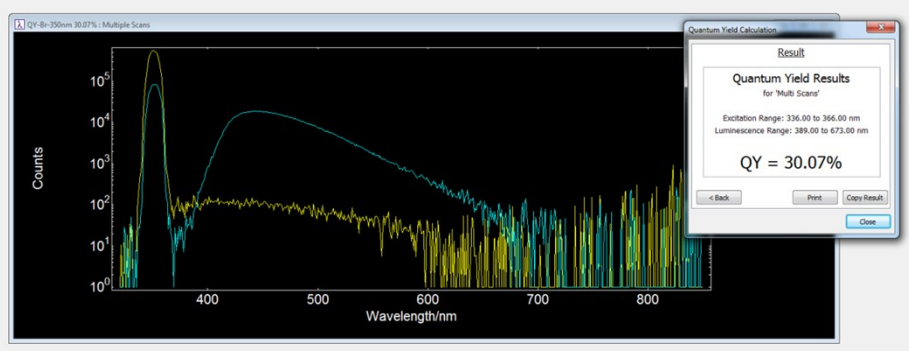

Fig. S7 quantum yield Φ of 4Br-TPE

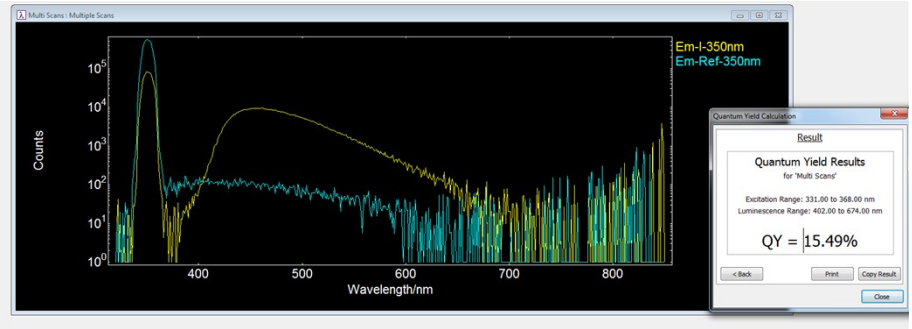

Fig. S8 quantum yield Φ of 4I-TPE

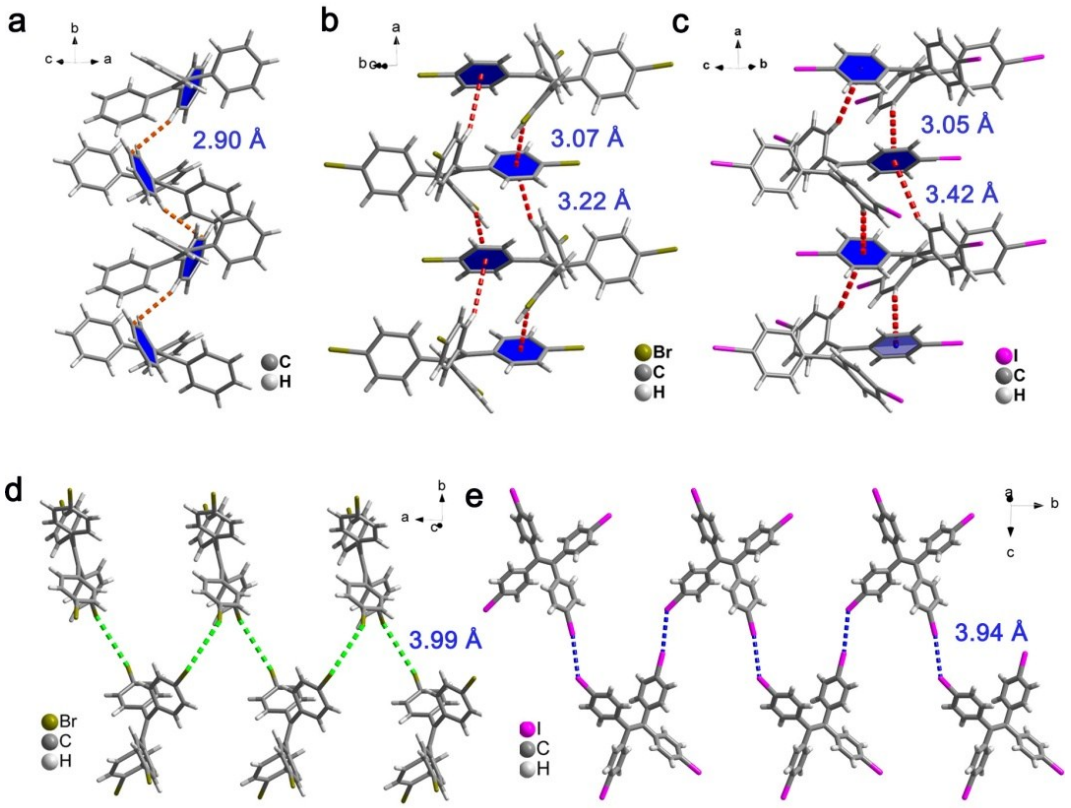

Fig. S9 a) C-H···C effect connected molecular chain along b-axis of TPE; b) double-chain structure connected by two C-H···π effects of 4Br-TPE; c) double-chain structure connected by two C-H···π effects of 4I-TPE; d) Br···Br interaction linking 4Br-TPE into a molecular chain along a-axis; e) I···I interaction linking 4I-TPE into molecular chain along b-axis.

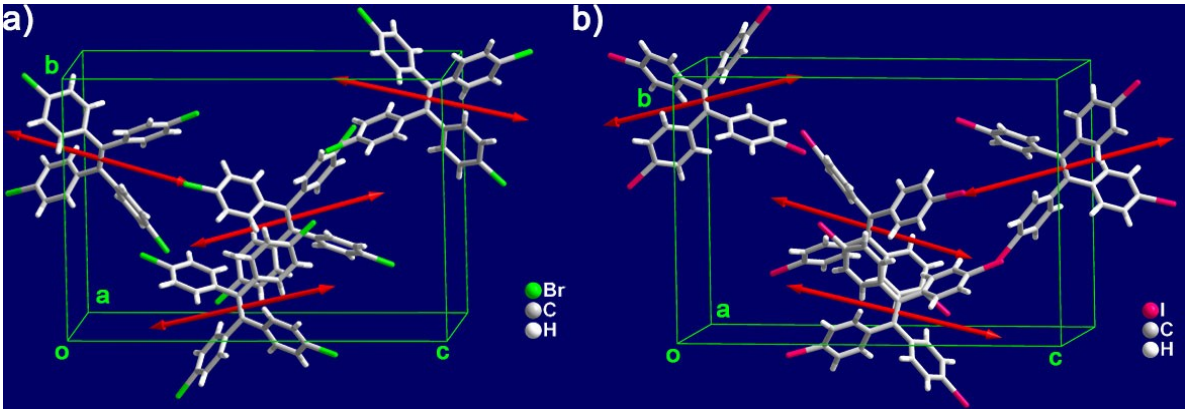

Fig. S10 Molecular arrangement in a unit cell of 4Br-TPE (a) and 4I-TPE (b) from single crystal X-ray diffraction analysis refinement; the red arrows indicate the orientation of transition dipoles.

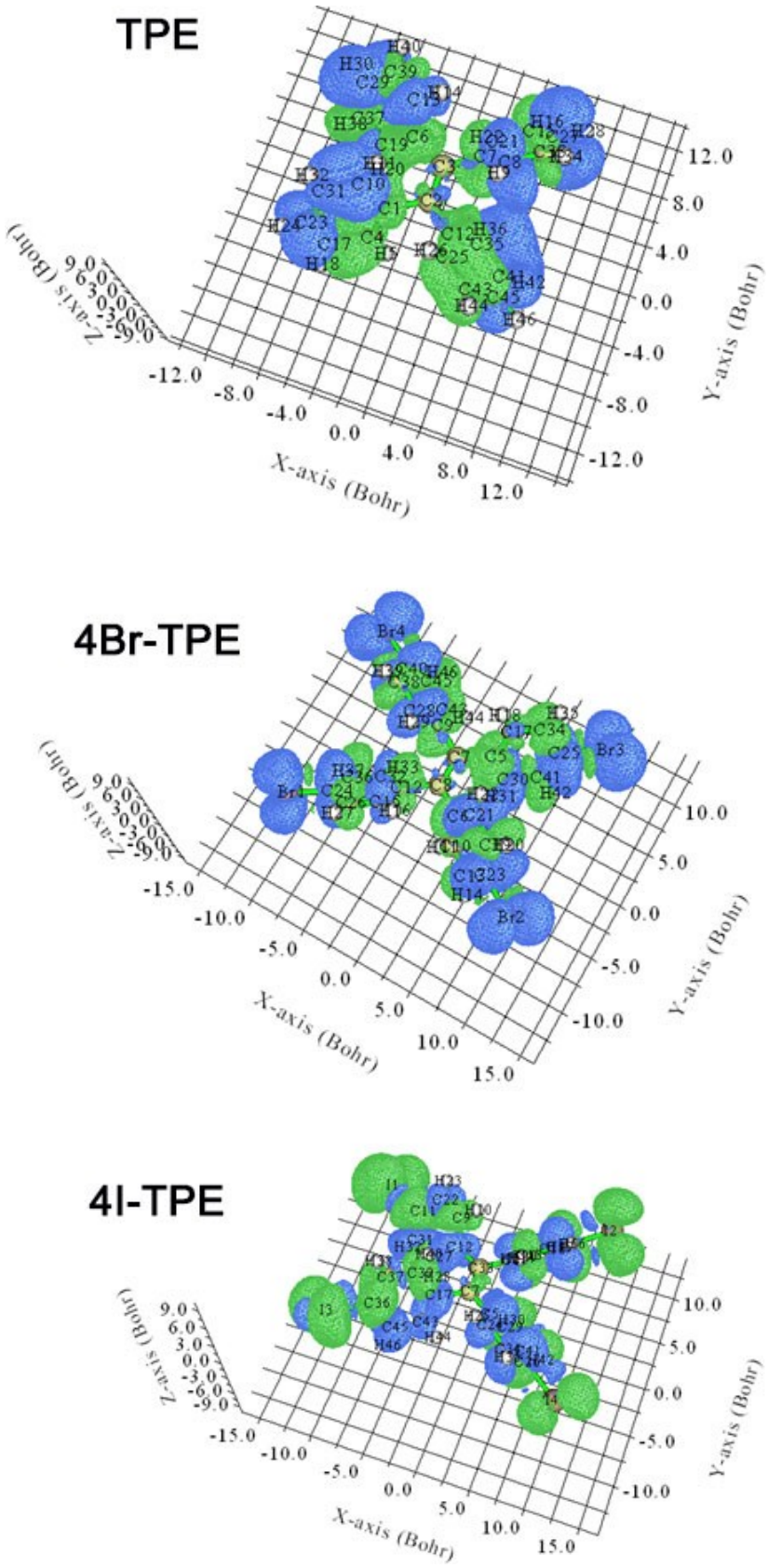

Fig. S11 The calculated transition dipole by Gaussian 09 software package.