Supporting Information

A Lanthanide Luminescence Sensor for Detection of 4-nitrophenol in Aqueous media

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Contents

Materials and Physical Measurements

All the reagents, $Ln(NO_3)_3 \cdot 6H_2O$ used were purchased from Aladdin Reagent (Shanghai) Co., Ltd. without further purification. The elemental analysis was obtained through the Thermo Flash 2000 elemental analyzer. The infrared spectrum was measured by Therrno Mattson FTIR spectrometer, and the wave number range was 4000~400 cm^{-1}. The powder X-ray diffraction (PXRD) patterns were recorded by X-ray diffractometer (Rigaku D / Max 2200PC) in the 2θ range of 5°~50°. On the TGA/NETZSCH STA449C instrument, the thermal analysis were performed from 30°C to 800°C at a heating rate of 10°C min^{-1} under N_2 flow. The single crystal data and diffraction crystal module of Mercury (Hg) program version 3.10 was used to simulate the PXRD mode of complexes. Luminescence excitation and emission spectra for samples were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Japan) with excitation and emission slits of 2.5 and 2.5 nm, respectively. For solid samples determination, the compacted solid samples with a thickness of 1 mm was placed between quartz plates. The phosphorescence spectra of **Gd-[2]c** in frozen solution at 77 K and lifetime measurements at 298 K were determined by an Edinburgh FLS920 single-photon-counting spectrometer equipped with a continuous Xe900 xenon lamp. The decay curves of **Tb-[2]c** and **ZnTb-[2]c** were measured under the same determination conditions and were fitted with a monoexponential function to obtain the best results. The overall quantum yield was determined on the basis of an absolute method.

Details of Single Crystal X-ray Diffraction

Suitable block crystals of **Tb-[2]c** was coated with perfluoropolyether oil before mounting. Intensity data for the aligned crystals of all the compounds were recorded at 173.20(10) K employing Bruker SMART APEX II CCD diffractometer equipped with a Cu Kα radiation (λ= 1.5718 Å) source. No crystal decay was observed during the data collections. The frames were integrated with the Bruker SAINT software package using a narrowframe algorithm.[1] Multi-scan empirical absorption corrections was applied using SADABS[2]. The structure was solved by direct methods and refined by full-matrix least-squares methods with a suite of SHELX 2014 programs via the Olex2 interface.[3] The

hydrogen atom's positions were calculated after each cycle of refinement with SHELXL using a riding model for each structure, with C–H distance of 0.93 or 0.96 Å, while Uiso(H) values were set equal to 1.2 Ueq of the parent carbon atom. The non-H atoms were refined anisotropically. The H atoms were placed in calculated positions and refined by using a riding model. The severely disordered solvents molecules in **Tb-[2]**c were removed by SQUEEZE during the structural refinements.[4] For details about the squeezed material, see cif data in Supporting Information. Therefore, solvent molecules which were determined on the basis of TGA analysis, elemental microanalysis were added to the molecular formula of **Tb-[2]**c. A summary of structural and refinement details for all were given in Table S1. Selected bond lengths and angles were given in Table S2. Crystallographic diagrams were drawn using the DIAMOND software package.[5]

Table S1. Crystal data and structure refinement parameters for **Tb-[2]**c.

CCDC No	2171975
Empirical formula	$C_{40}H_{42}N_8O_{20}Tb_2$
Temperature (K)	173.20(10)
formula_weight	1272.65
Diffraction	CuKα (λ = 1.54184)
Crystal system, Space group	Monoclinic, P2$_1$/n
Unit cell dimensions	a = 15.0020(5) Å, b = 15.5597(5) Å, c = 24.3406(9) Å, β = 99.222(4) °
V/Å^3, Z	5608.3(3), 4
D_{calcd}/Mg m^{-3}	1.507
μ/mm^{-1}	12.873
$F(000)$	2512.0
Θ range for data collection	7.358° ~ 142.14°
index ranges, hkl	-18 ≤ h ≤ 18, -18 ≤ k ≤ 13, -24 ≤ l ≤ 29
Independent reflections (R_{int})	0.0463
Completeness	97.6%
Reflections unique / collected	10602/20418
Data / restraints / params	10602/7/631
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0483, wR_2 = 0.1162
R indices (all data)	R_1 = 0.0697, wR_2 = 0.1307

Table S2. Selected bond lengths (Å) for **Tb-[2]**c.

Tb1–O1	2.335(4)	Tb1–O2	2.313(4)	Tb1–O8	2.345(4)	Tb1–O11	2.475(4)
Tb1–O12	2.208(4)	Tb1–O16	2.452(5)	Tb1–O15	2.511(4)	Tb1–N5	2.531(5)
Tb2–O1	2.350(4)	Tb2–O4	2.460(4)	Tb2–O5	2.236(4)	Tb2–O8	2.332(4)
Tb2–O9	2.303(4)	Tb2–O18	2.454(4)	Tb2–O19	2.498(4)	Tb2–N2	2.502(5)

Table S3 Shape calculation results of Tb^{III} in **Tb-[2]c**.

		Tb2
Octagon(OP-8)	0.2502	0.2560
Heptagonal pyramid(HPY-8)	0.1584	0.1576
Hexagonal bipyramid(HBPY-8)	0.1645	0.1688
Cube(CU-8)	0.1579	0.1551
Square antiprism(SAPR-8)	0.0813	0.0794
Triangular dodecahedron(TDD-8)	0.0728	0.0726
Johnson gyrobifastigium J26(JGBF-8)	0.1811	0.1896
Johnson elongated triangular bipyramid J14(JETBPY-8)	0.2699	0.2708
Biaugmented trigonal prism J50(JBTPR-8)	0.0709	0.0728
Biaugmented trigonal prism(BTPR-8)	0.0767	0.0780
Snub diphenoid J84(JSD-8)	0.0896	0.0948
Triakis tetrahedron(TT-8)	0.1557	0.1533
Elongated trigonal bipyramid(ETBPY-8)	0.2440	0.2437
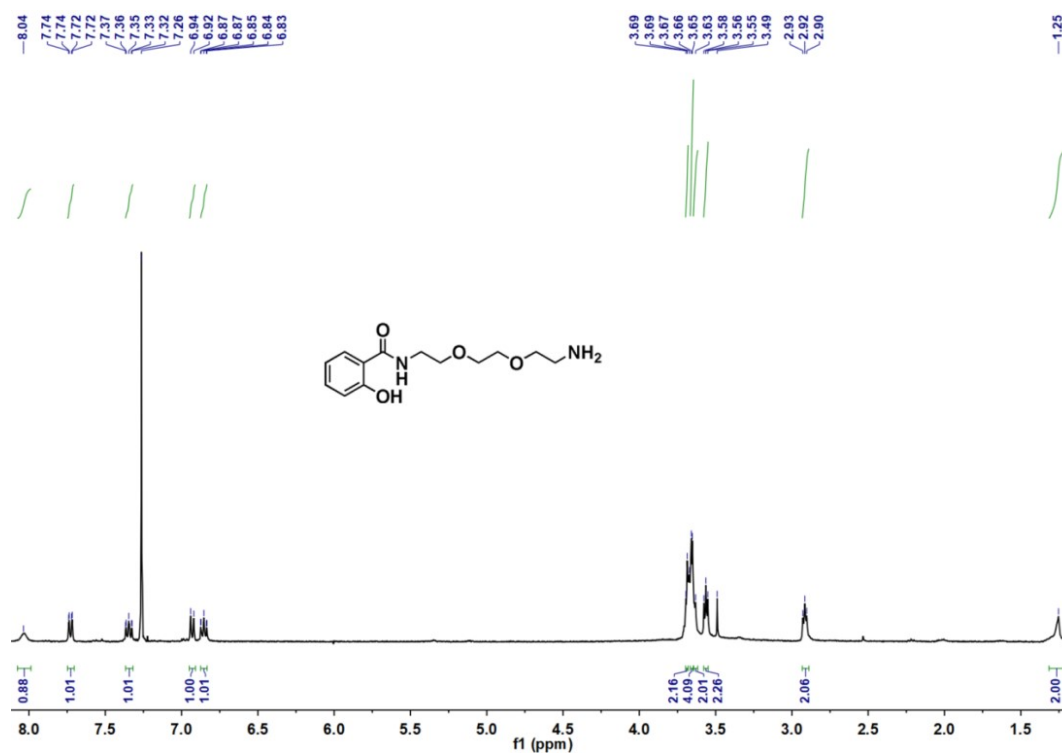
Figure S1. ^{1}H NMR(500 MHz, CDCl$_3$) spectra of mono-amidated 1,2-Bis(2-aminoethoxy)ethane.
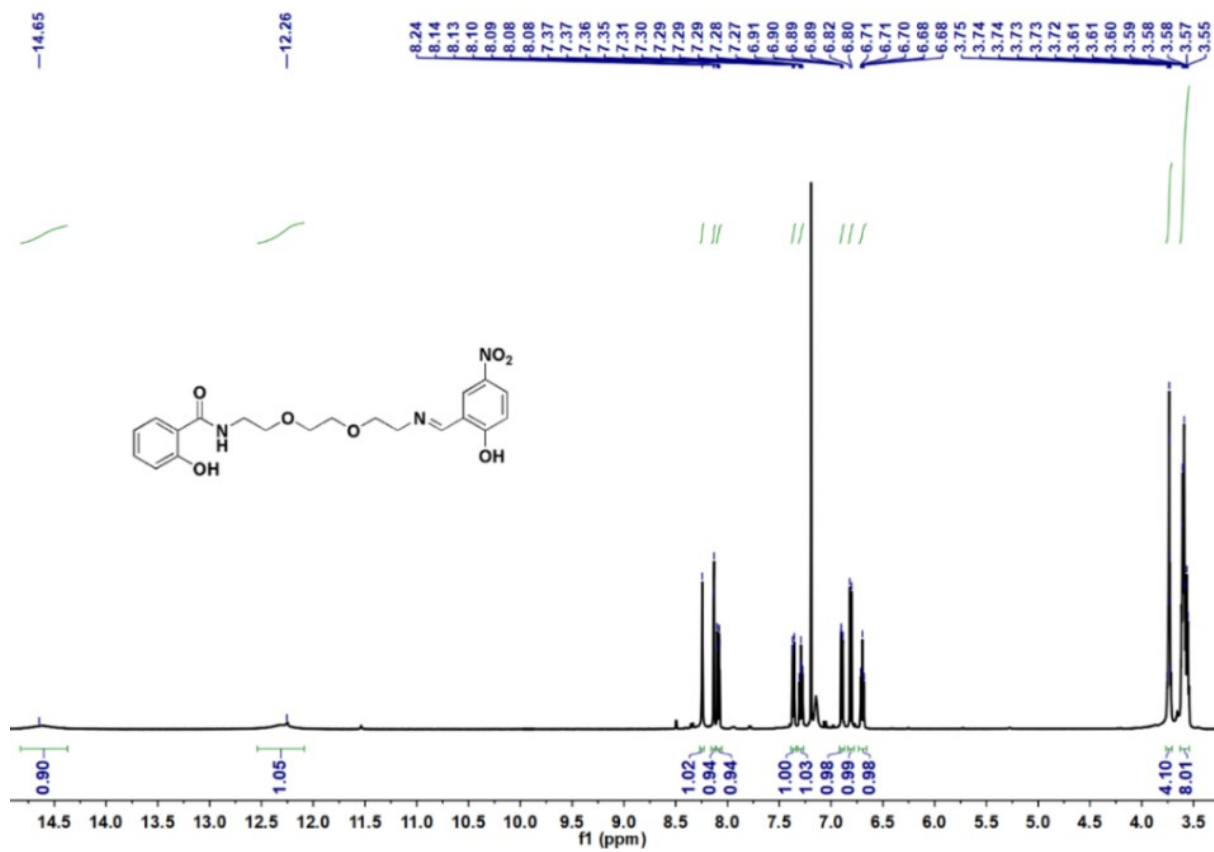
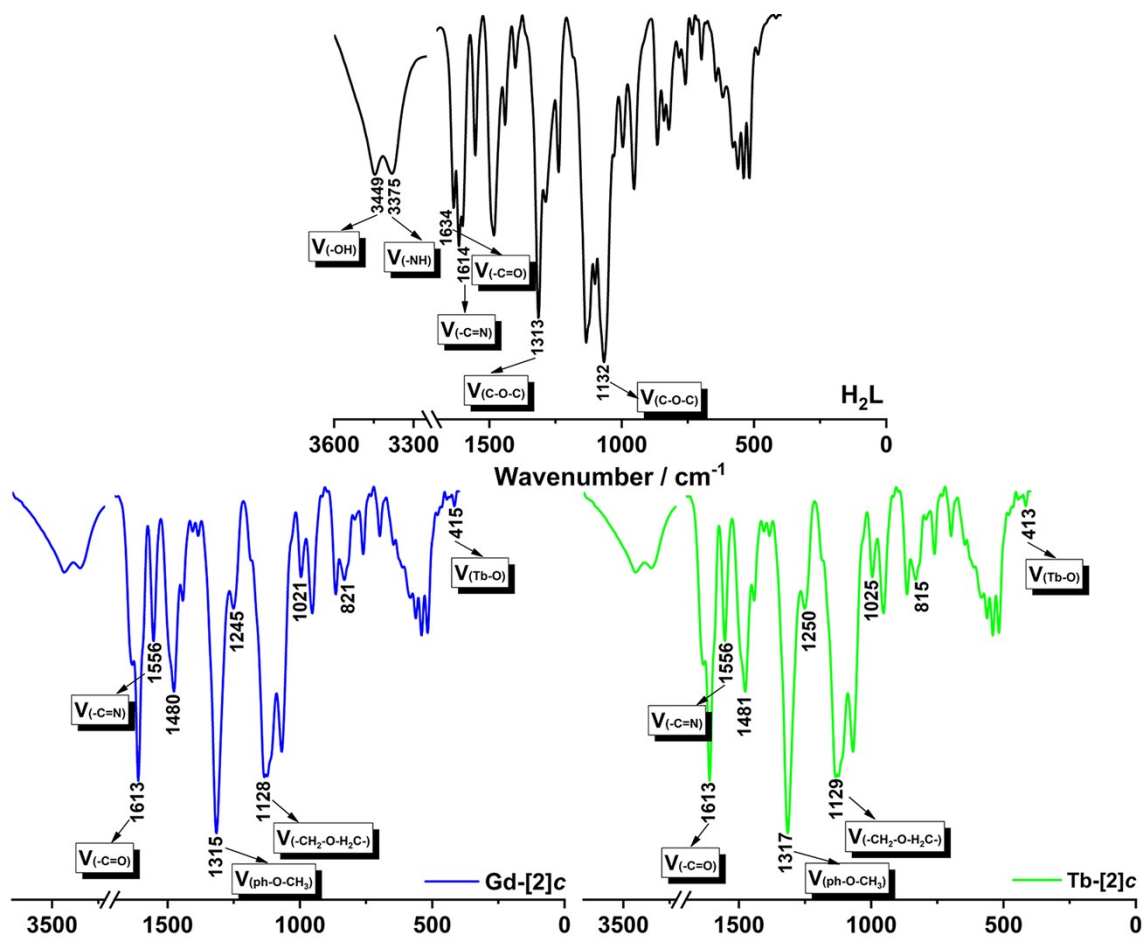Figure S2. ^{1}H NMR(500 MHz, CDCl$_3$) spectra of **H$_2$L**.

Figure S3. IR spectra of **H₂L**, **Gd-[2]***c*, **Tb-[2]***c* in solid state.
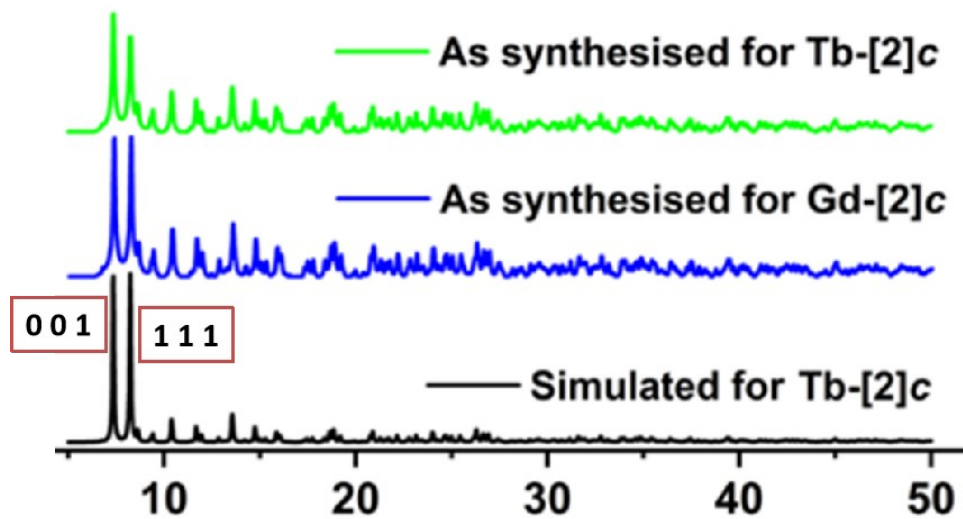

Figure S4. PXRD patterns of as-synthesized **Gd-[2]***c*, **Tb-[2]***c* and that simulated for **Tb-[2]***c*.
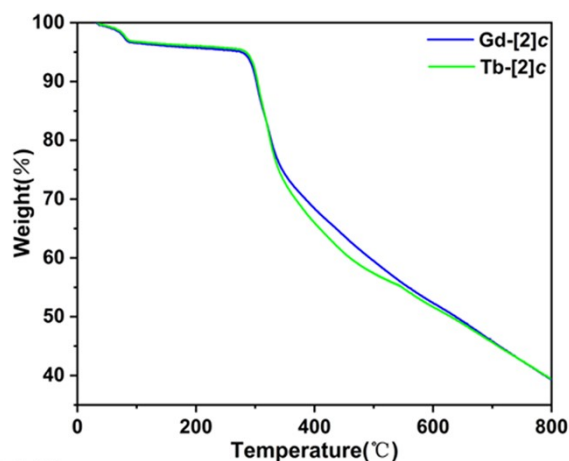
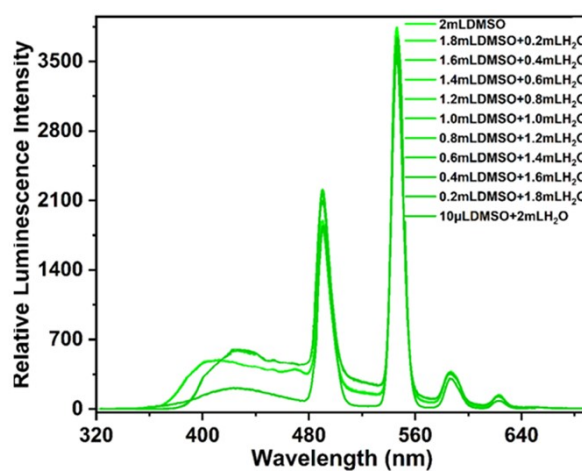Figure S5. TGA curves of **Gd-[2]c**, **Tb-[2]c** from 25 ~ 800°C.

Figure S6. The emission spectra of **Tb-[2]c** in different DMSO+ H_2O solutions upon excited at λ_{ex} = 320 nm).
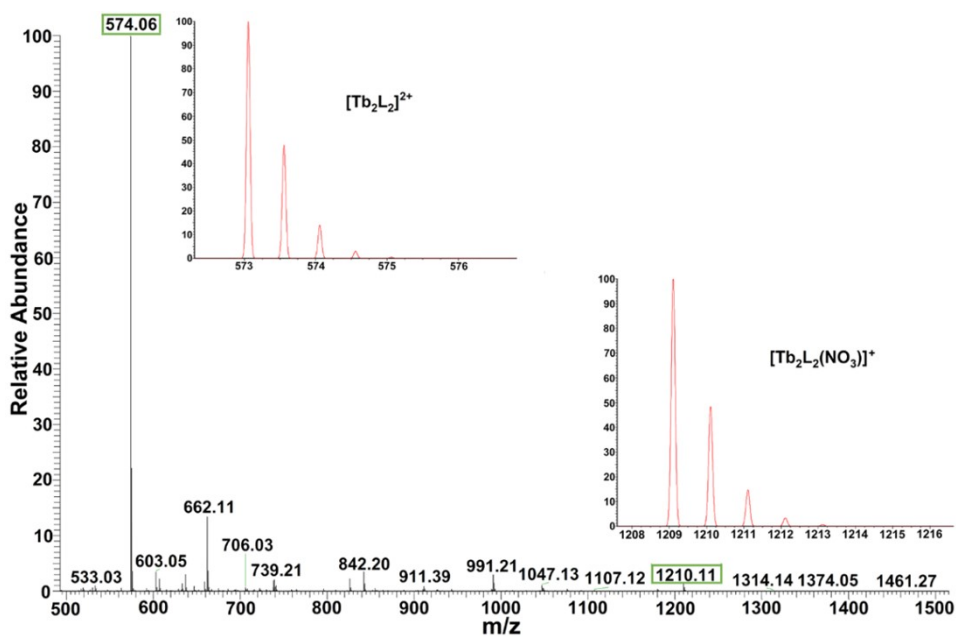

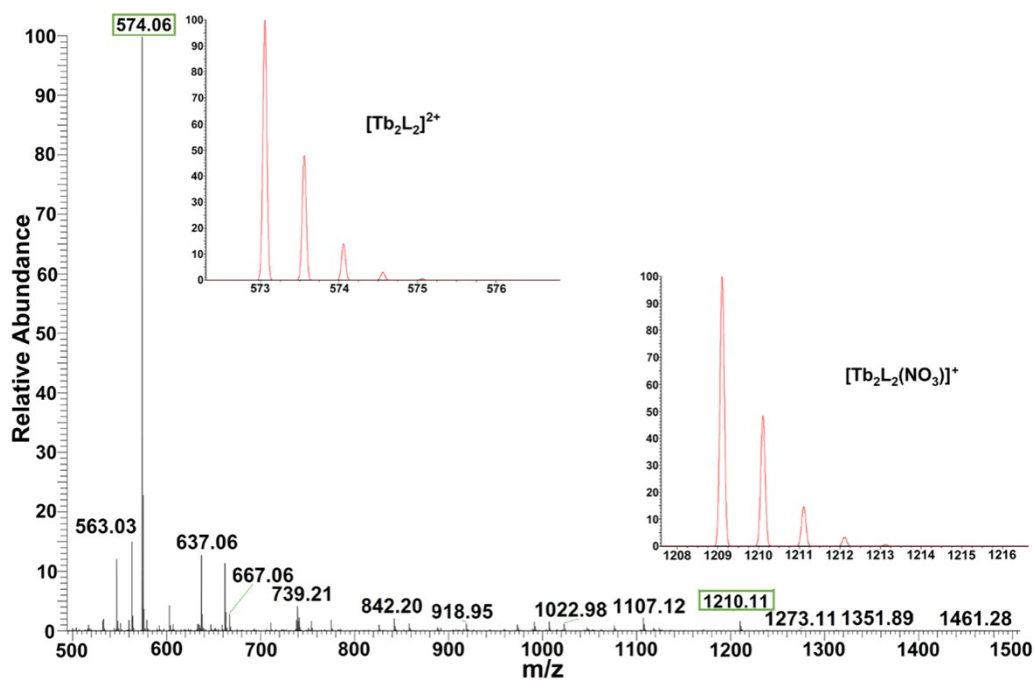Figure S7. ESI mass spectrum of Tb-[2]c H_2O-DMSO solution(V_{H2O} :V_{DMSO} = 99.5: 0.5) .

Figure S8. ESI mass spectrum of **Tb-[2]c** H_2O-DMSO solution(V_{H2O} : V_{DMSO} = 99.5: 0.5) upon addition of 4-NP.
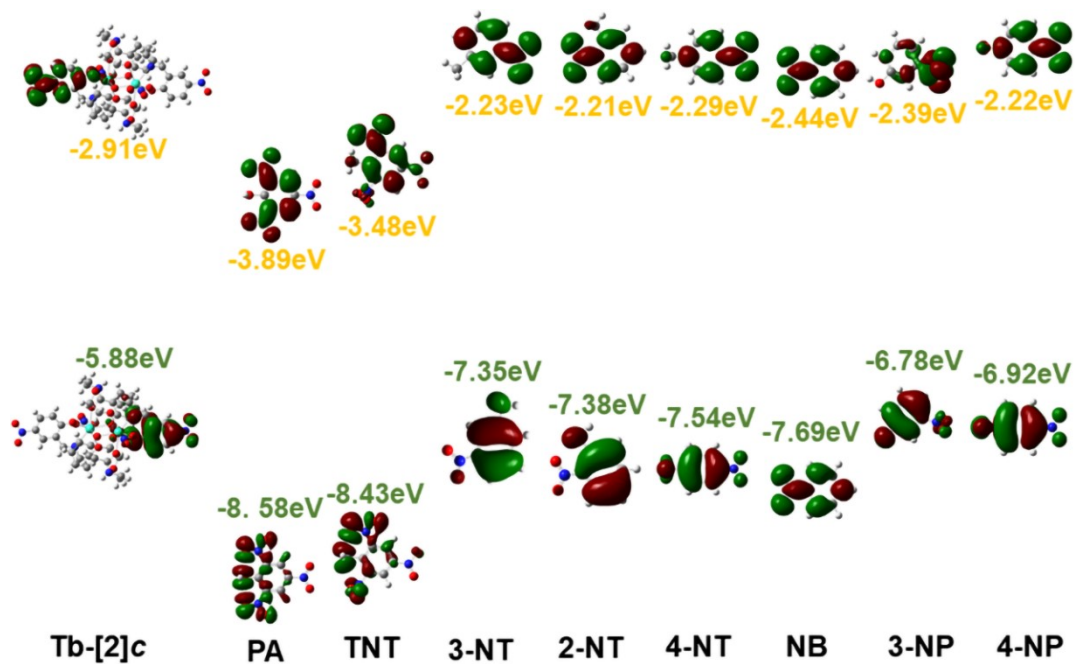

Figure S9. Pictorial representation of the excited state electron transfer from the LUMO to HOMO of **Tb-[2]c** and various nitroaromatics.

Reference

1. SAINT Plus, (Version 7.03); Bruker AXS Inc.: Madison, WI, **2004**.

2. SADABS, version 2.03; Bruker AXS Inc. Madison, WI, **2002**.

3. O.V. Dolomanov, L.J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, **2009**, *J. Appl. Cryst.* 42, 339–341.

4. A. L. Spek, The calculation of the solvent-accessible was performed by using the PLATON software (similarly herein after) *J. Appl. Crystallogr*. **2003**, 36, 7.

5. DIAMOND, Visual Crystal Structure Information System, version 3.1; Crystal Impact: Bonn, Germany, **2004**.