Supporting Information for

Synthesis of hydroxo-bridged Dy(III) dimers supported by crown ethers through C–H activation and oxygen-atom transfer of Me_3NO

Ziyi Gu,[a,b] Jun Li,[a,c] Xuan Zhang,[a,c] Yangjuan Li *[a] and Yu Gong [a]

[a] State Key Laboratory of Thorium Energy, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

[b] ShanghaiTech University, Shanghai 201210, China

[c] University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding Author (liyangjuan@sinap.ac.cn)

1 Crystallographic data

Table S1. Selected bond lengths (Å) and bond angles(deg) for complex **1**.

Atom	Atom	Length/Å
Dy(1)	O(4)	2.411(5)
Dy(1)	O(7)	2.416(4)
Dy(1)	O(3)	2.428(4)
Dy(1)	O(2)	2.401(5)
Dy(1)	O(1)	2.478(5)
Dy(1)	O(5)	2.416(5)
Dy(1)	O(8)	2.469(4)
Dy(1)	O(6)	2.375(4)
Dy(1)	N(1)	2.447(6)

Atom	Atom	Atom	Angle/°
O(4)	Dy(1)	O(3)	66.96(16)
O(4)	Dy(1)	O(1)	65.04(17)
O(7)	Dy(1)	O(8)	63.25(15)
O(2)	Dy(1)	O(3)	66.51(16)
O(2)	Dy(1)	O(1)	65.24(17)
O(5)	Dy(1)	O(8)	64.45(18)
O(6)	Dy(1)	O(7)	67.54(15)
O(6)	Dy(1)	O(5)	68.37(16)

Table S2. Selected bond lengths (Å) and bond angles(deg) for complex **2**.

Atom	Atom	Length/Å

Dy(1)	I(3)	2.9962(5)
Dy(1)	O(3)	2.389(4)
Dy(1)	O(2)a	2.426(3)
Dy(1)	O(2)	2.426(3)
Dy(1)	O(1)a	2.401(4)
Dy(1)	O(1)	2.401(4)
Dy(1)	N(1)	2.445(4)
Dy(1)	N(1)a	2.445(4)

Atom	**Atom**	**Atom**	**Angle/°**
O(3)	Dy(1)	O(2)	66.15(7)
O(3)	Dy(1)	O(2)a	66.15(7)
O(1)	Dy(1)	O(2)	66.08(13)
O(1)a	Dy(1)	O(2)a	66.08(13)
O(1)a	Dy(1)	O(1)	64.32(18)

Table S3. Selected bond lengths (Å) and bond angles(deg) for complex **3**.

Atom	**Atom**	**Length/Å**
Dy(1)	O(1)	2.216(3)
Dy(1)	O(1)a	2.228(2)
Dy(1)	O(2)	2.446(2)
Dy(1)	O(3)	2.521(2)
Dy(1)	O(4)	2.501(2)
Dy(1)	O(5)	2.457(2)
Dy(1)	N(1)	2.474(3)

Dy(1)	I(1)	3.1450(3)

Atom	Atom	Atom	Angle/°
O(2)	Dy(1)	O(3)	64.73(8)
O(4)	Dy(1)	O(3)	65.51(8)
O(5)	Dy(1)	O(4)	65.80(8)
O(2)	Dy(1)	O(5)	65.70(9)
Dy(1)	O(1)	Dy(1)a	109.45(10)

Table S4. Selected bond lengths (Å) and bond angles(deg) for complex **4**.

Atom	Atom	Length/Å
Dy(1)	O(1)	2.190(5)
Dy(1)	O(1)a	2.253(4)
Dy(1)	O(3)	2.430(4)
Dy(1)	O(5)	2.453(5)
Dy(1)	O(2)	2.410(4)
Dy(1)	O(4)	2.446(4)
Dy(1)	O(6)	2.516(5)
Dy(1)	N(1)	2.468(6)

Atom	Atom	Atom	Angle/°
O(2)	Dy(1)	O(3)	64.17(15)
O(3)	Dy(1)	O(4)	66.13(16)
O(4)	Dy(1)	O(5)	63.28(16)
O(5)	Dy(1)	O(6)	64.03(17)

O(2)	Dy(1)	O(6)	64.29(16)
Dy(1)	O(1)	Dy(1)a	110.2(2)

Table S5. Selected bond lengths (Å) and bond angles(deg) for complex **5**.

Atom	**Atom**	**Length/Å**
Dy(1)	O(5)	2.388(6)
Dy(1)	O(4)	2.424(7)
Dy(1)	O(6)	2.402(7)
Dy(1)	O(8)	2.414(7)
Dy(1)	O(2)	2.411(6)
Dy(1)	O(7)	2.419(8)
Dy(1)	O(9)	2.477(8)
Dy(1)	O(3)	2.472(6)
Dy(1)	O(1)	2.323(7)

Atom	**Atom**	**Atom**	**Angle/°**
O(2)	Dy(1)	O(3)	64.6(2)
O(4)	Dy(1)	O(3)	63.5(2)
O(5)	Dy(1)	O(4)	66.6(2)
O(5)	Dy(1)	O(2)	68.1(2)
O(6)	Dy(1)	O(7)	67.7(3)
O(8)	Dy(1)	O(7)	67.4(2)
O(8)	Dy(1)	O(9)	65.8(2)
O(6)	Dy(1)	O(9)	64.8(2)

Table S6. Selected bond lengths (Å) and bond angles(deg) for complex **6**.

Atom	Atom	Length/Å
Dy(1)	O(1)	2.305(3)
Dy(1)	O(2)	2.366(2)
Dy(1)	O(3)	2.3886(17)
Dy(1)	O(3)a	2.3886(17)
Dy(1)	O(4)	2.3482(18)
Dy(1)	O(4)a	2.3482(18)
Dy(1)	N(1)	2.458(2)
Dy(1)	N(1)a	2.458(2)

Atom	Atom	Atom	Angle/°
O(2)	Dy(1)	O(3)	67.19(4)
O(2)	Dy(1)	O(3)a	67.19(4)
O(4)	Dy(1)	O(3)	66.94(6)
O(4)a	Dy(1)	O(3)a	66.94(6)
O(4)	Dy(1)	O(4)a	64.36(9)

2 Powder X-ray diffraction

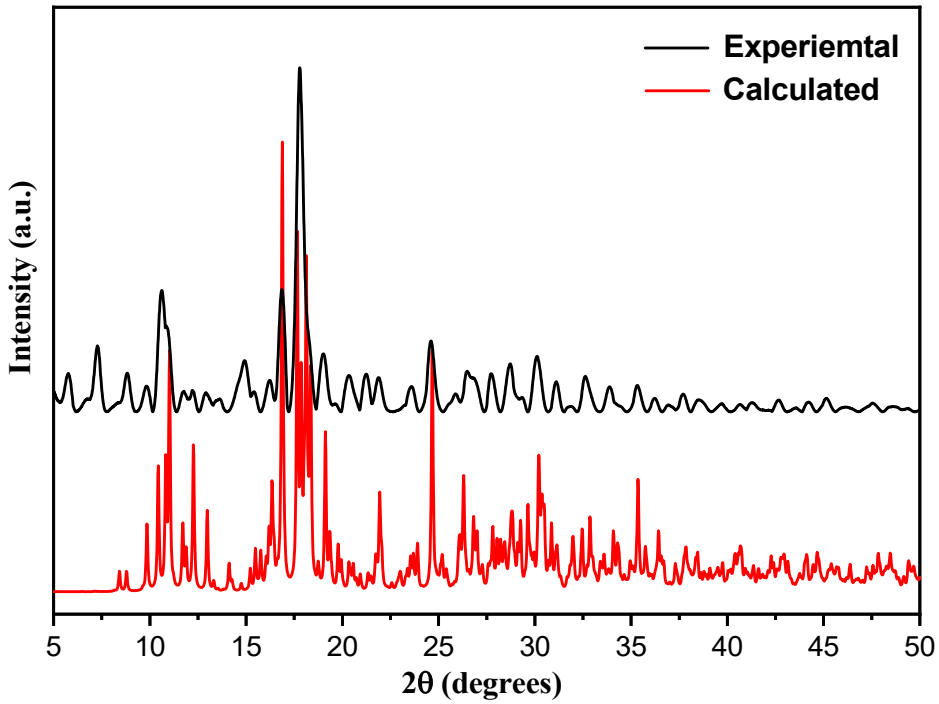


Fig. S1. PXRD pattern calculated from single-crystal data of [Dy(12-crown-4)$_2$(CH$_3$CN)]I$_3$ (**1**) compared to experimental data of the precipitate isolated.

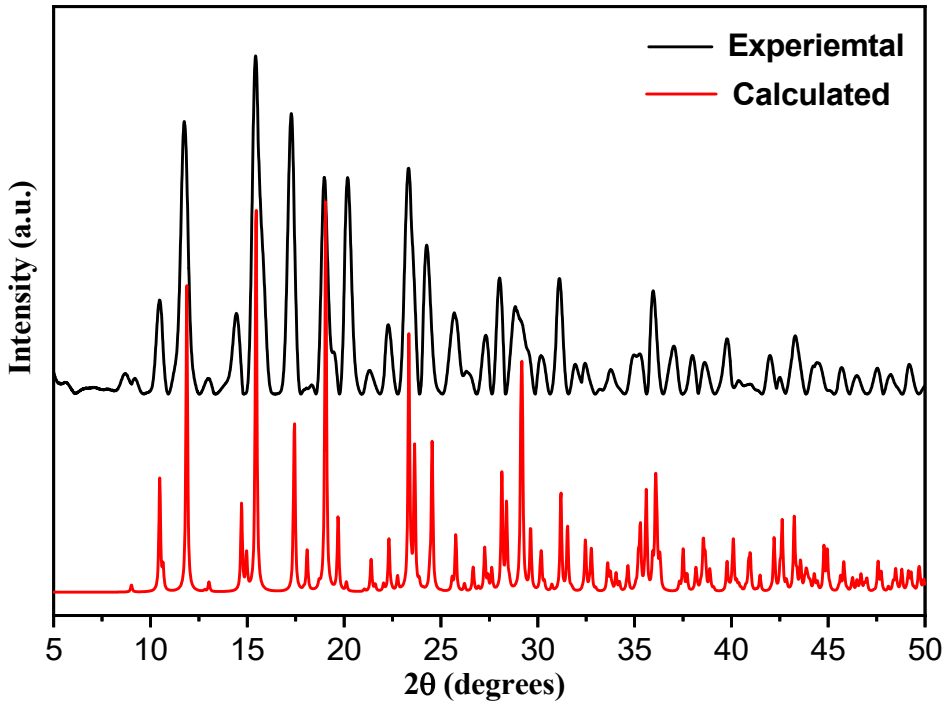


Fig. S2. PXRD pattern calculated from single-crystal data of [Dy(15-crown-

5)($CH_3CN)_2I]I_2$ (**2**) compared to experimental data of the precipitate isolated.

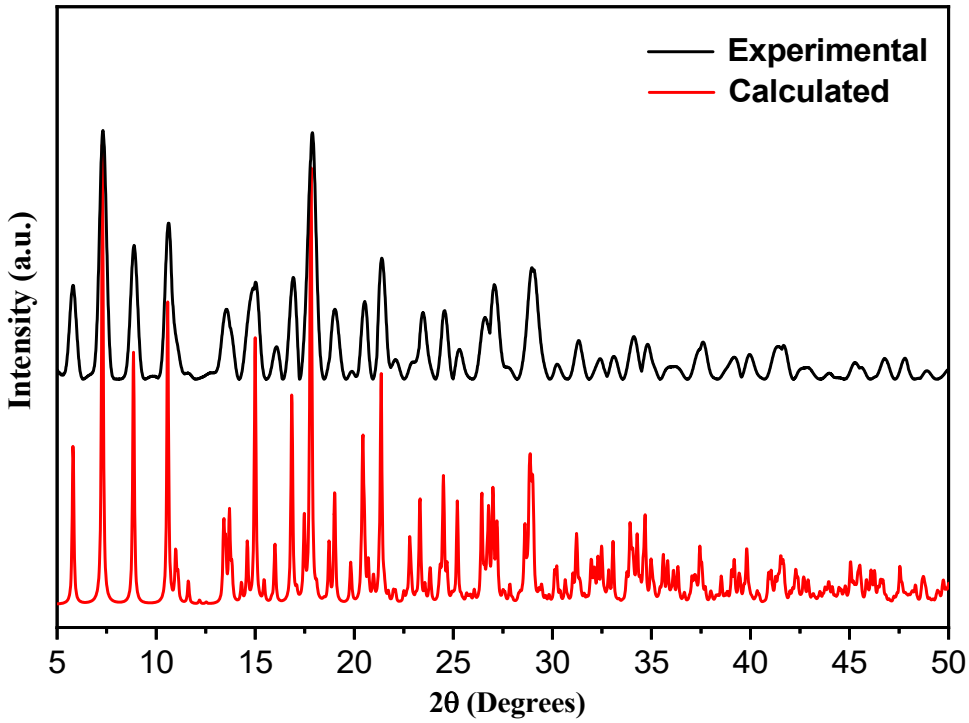


Fig. S3. PXRD pattern calculated from single-crystal data of [Dy(12-crown-4)$_2$(H_2O)]($CH_3CN)_3I_3$ (**5**) compared to experimental data of the precipitate isolated.

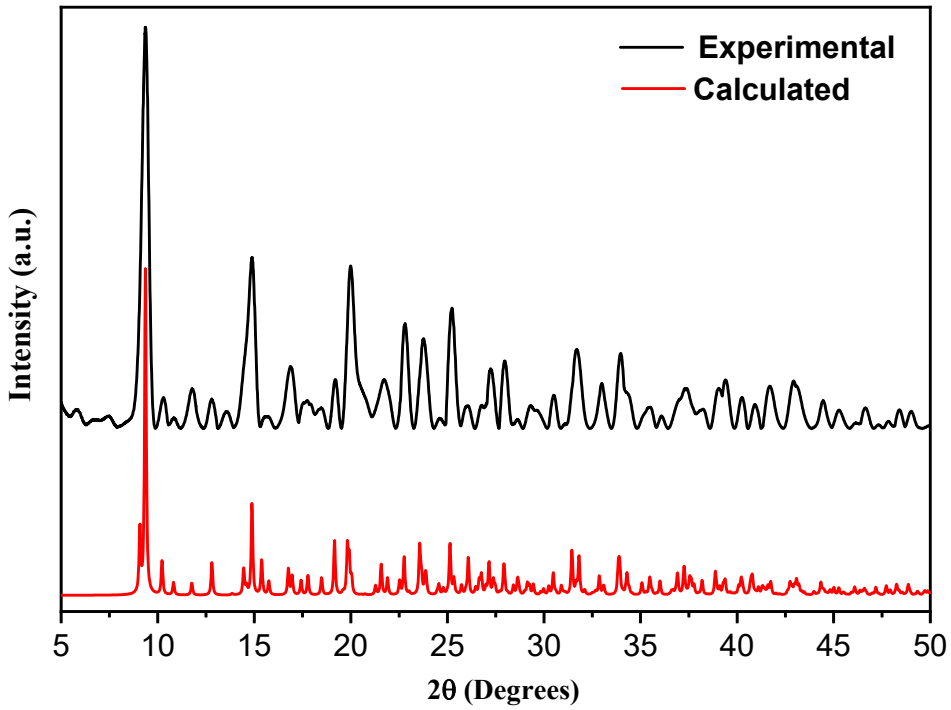


Fig. S4. PXRD pattern calculated from single-crystal data of [Dy(12-crown-4)(μ-OH)(CH_3CN)I]$_2$$I_2$($CH_3CN$)$_2$ (**3**) compared to experimental data obtained from the crystal formed by the reaction of complex **5** with Me_3NO.

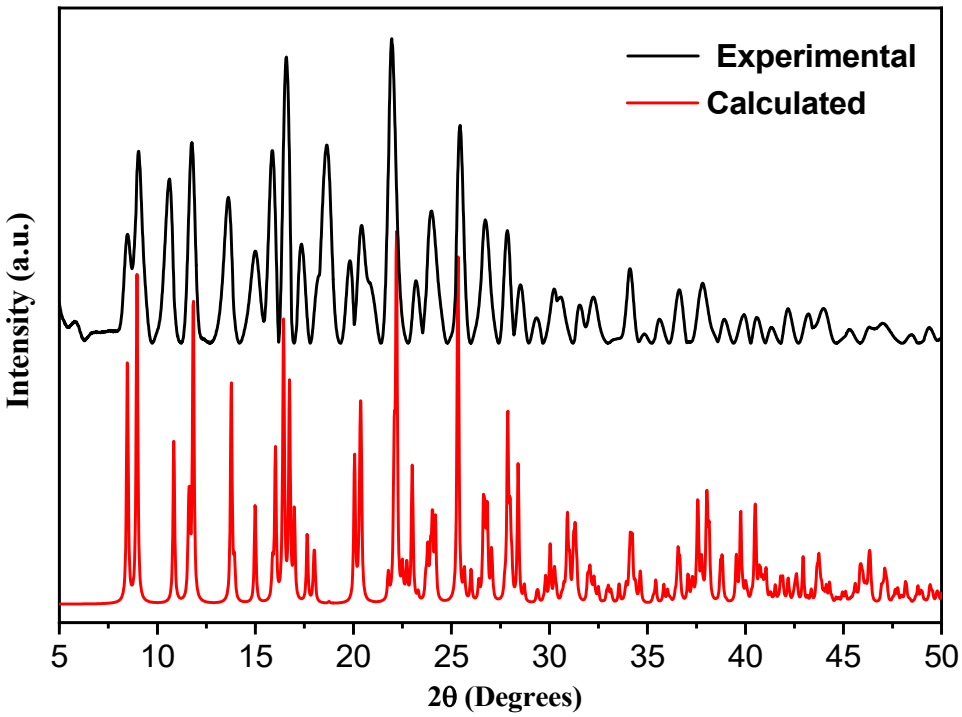


Fig. S5. PXRD pattern calculated from single crystal data of [Dy(15-crown-5)(μ-OH)(CH_3CN)]$_2$$I_4$ (**4**) compared to experimental data obtained from the crystal formed by the reaction of complex **6** with Me_3NO.

3 ^{1}H NMR spectra

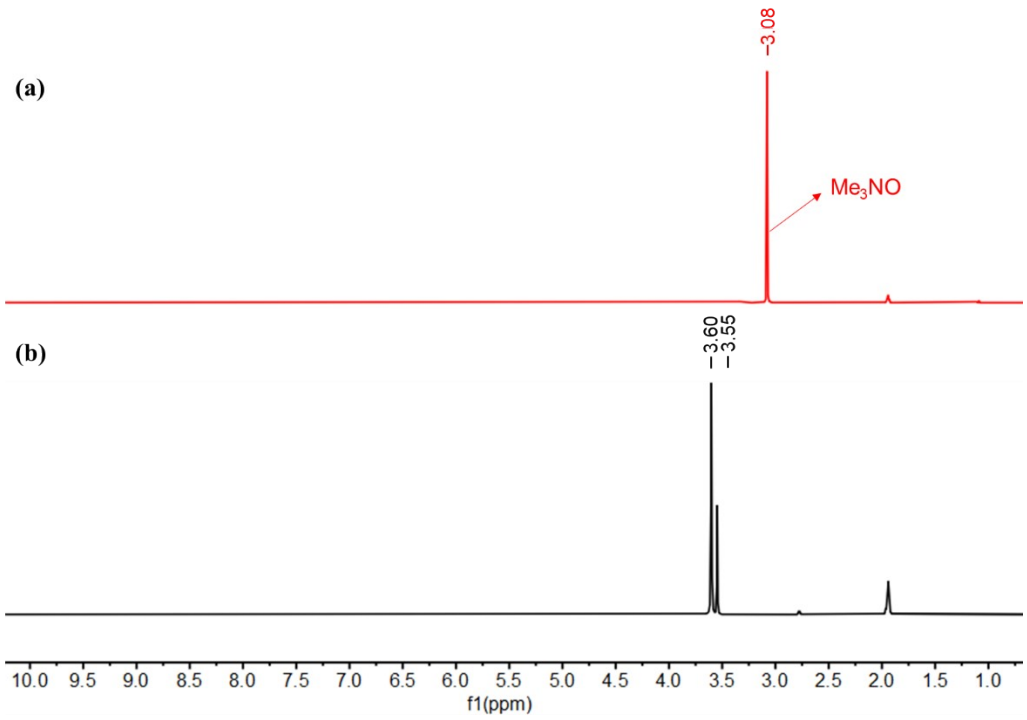


Fig. S6. ^{1}H NMR spectra of Me_3NO (a) and the soluble fraction of the non-volatile residues obtained from the acetonitrile solution where complex **3** was formed (b) in CD_3CN.

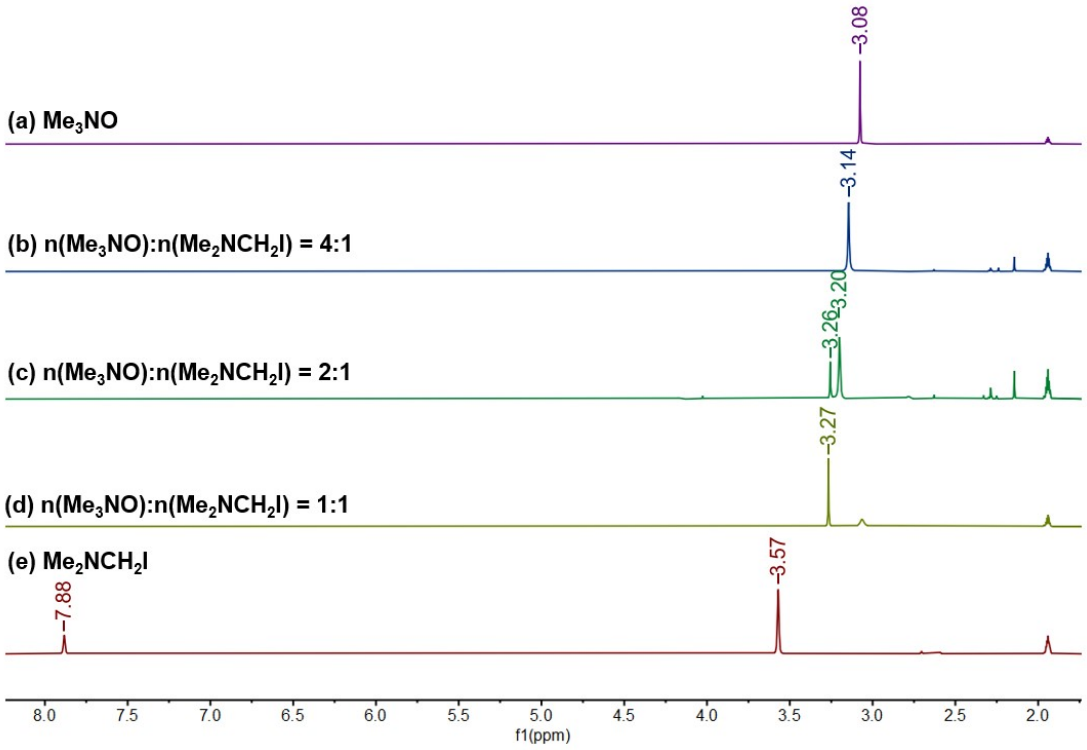
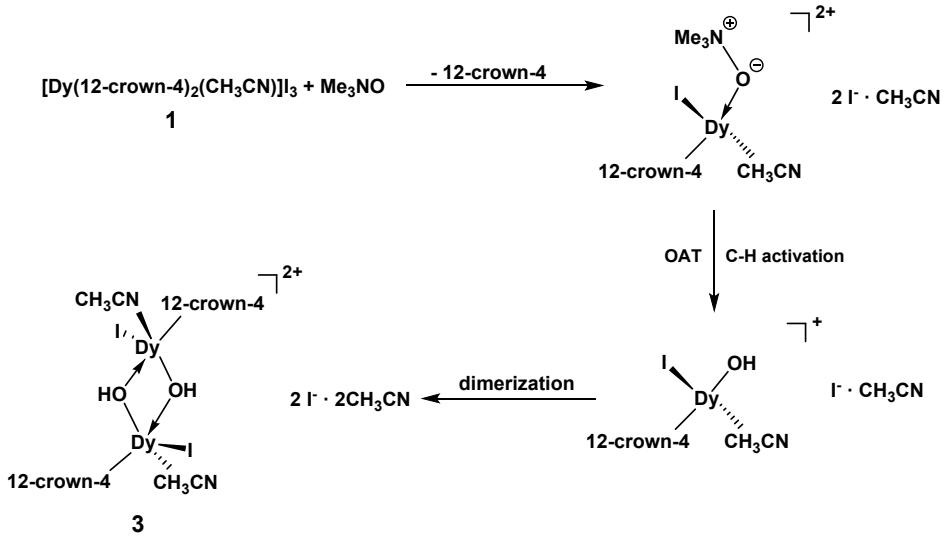


Fig. S7. ^{1}H NMR spectra of Me_3NO and Me_2NCH_2I in different ratio in CD_3CN.

4 Plausible reaction mechanism



Scheme S1 Proposed reaction mechanism for the formation of complex **3**. Me_3NO first replaces one molecule of 12-crown-4 in complex **1** to form an adduct of Dy(III). An intermediate coordinated with a hydroxo ligand is then formed through C–H activation along with OAT of Me_3NO, which is further dimerized to form complex **3**.