Electronic Supplementary Information

for

Substituent Effects in Cation-π Interactions. Recognition of Tetramethylammonium Chloride by Uranyl-Salophen Receptors.

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Materials. Salophen-UO_2 complexes **1** (X= CH_3O, Me, Br and NO_2) were available from a previous investigation (ref. 9 in the main text). Tetramethylammonium chloride, (TMA)Cl, and triphenylmethane, TPM, were purchased from Sigma-Aldrich; (TMA)Cl was re-crystallized before use as described below before use.

NMR Studies. ^{1}H-NMR spectra were recorded on a 250 MHz Bruker Advance spectrometer. All ^{1}H-NMR titrations were run at 298 K following a published procedure (ref. 11 in the main text). Each tested receptor was washed with $CHCl_3$ (amylene stabilized, three times) prior to the experiment. (TMA)Cl was re-crystallized from MeOH and dried before its use. Stock solution of (TMA)Cl was obtained by adding an excess of it in a $CDCl_3$ solution. After 12-18 hours of stirring, the solution was filtrated, and the (TMA)Cl concentration was measured by ^{1}H-NMR. Triphenylmethane was used as an internal standard. The (TMA)Cl stock solution was then diluted final concentration range 0.15-0.40 mM

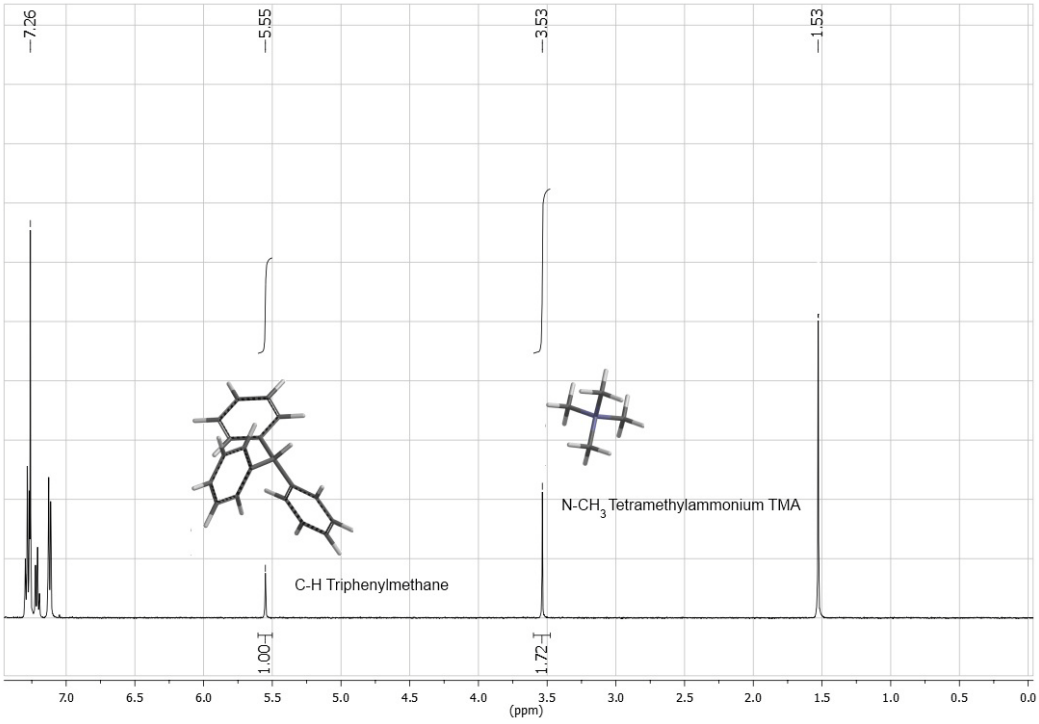

Figure 1S. Example of (TMA)Cl concentration measurement by signals' integral comparison with an internal standard TPM.

Titrations Plots.

Titration plots for Salophen-UO_2 complexes **1 (X= H)** and Salophen-UO_2 complexes **3** were already reported in reference 10b and 9 (see manuscript), respectively. Reported values are σ-weighted averages from two independent runs using equation (1):

$$K = (\sum_{i}^{N} \frac{K_i}{\sigma^2{}_i})/(\sum_{i}^{N} \frac{1}{\sigma^2{}_i}) \qquad (1)$$

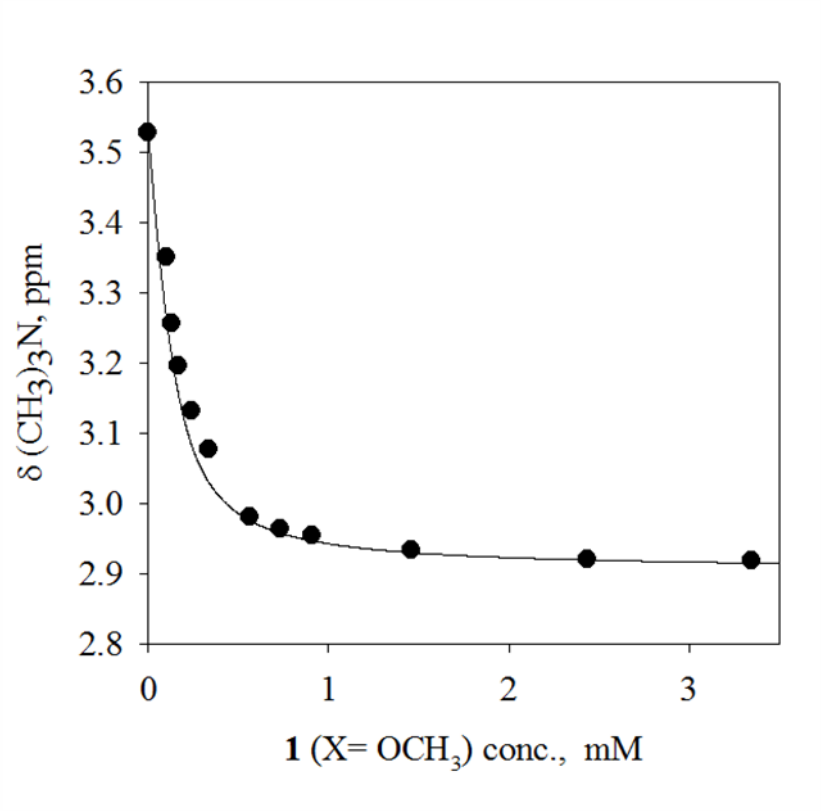

Figure 2S. ^{1}H NMR titration of 0.15 mM (TMA)Cl with receptor **1** (X =OCH_3) in $CDCl_3$ at 25°C.

K, X= OCH_3

first run: 16900 ± 600

second run: 18100 ± 500

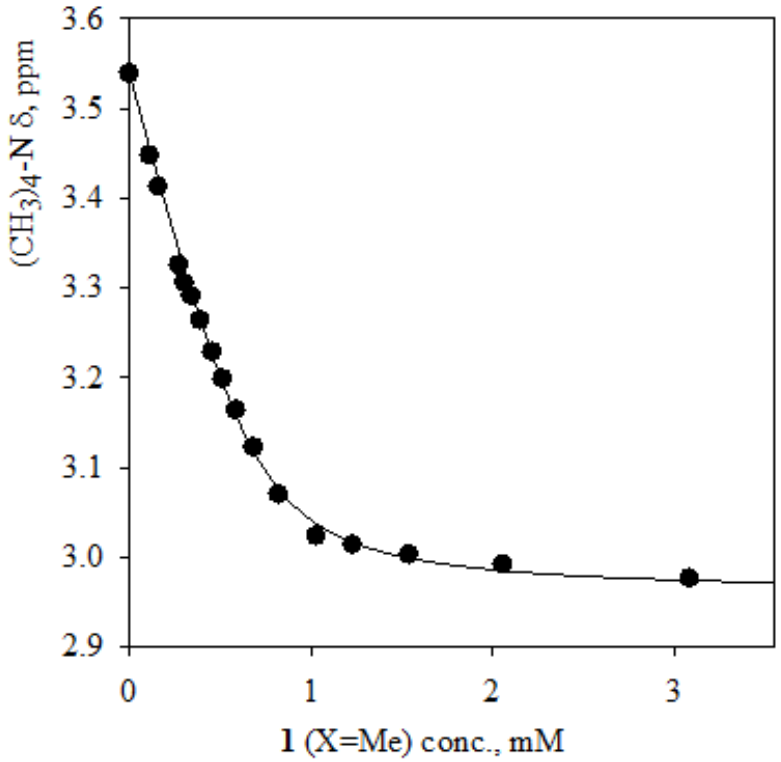

Figure 3S. ^{1}H-NMR titration of 0.40 mM (TMA)Cl with receptor **1** (X= Me) in CDCl3 at 25°C.

K, X= Me

first run: 14150 ± 850

second run: 16200 ± 1000

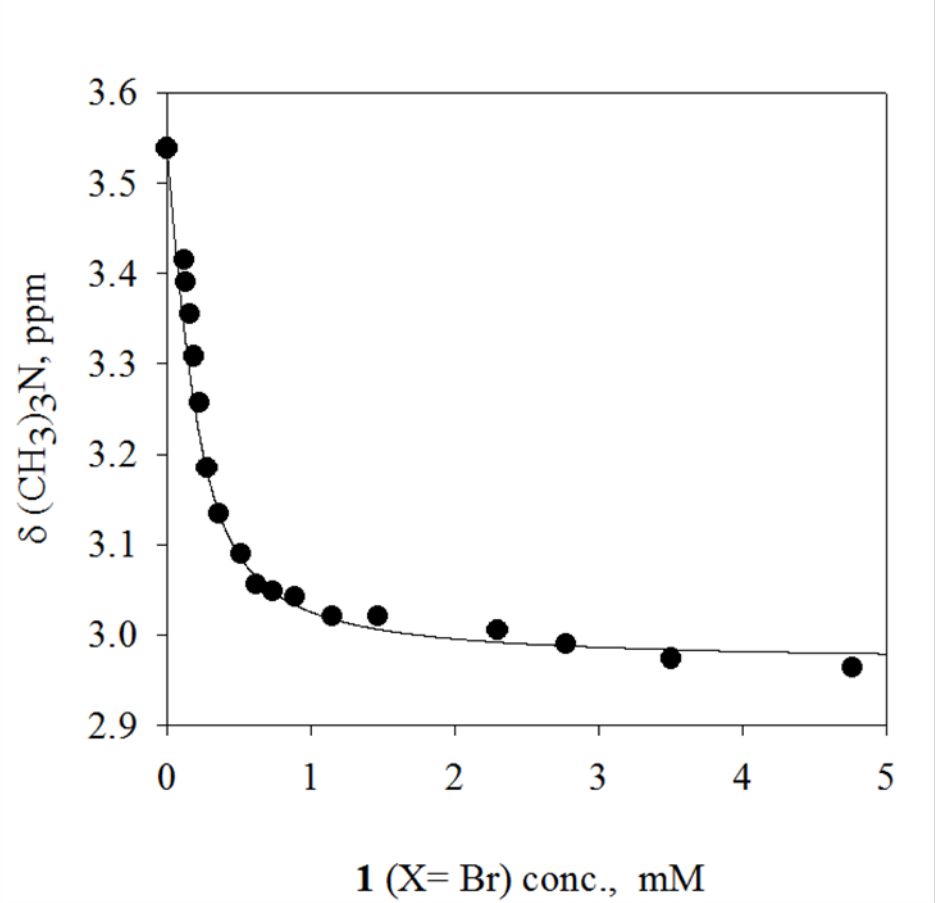

Figure 4S. ^{1}H NMR titration of 0.20 mM (TMA)Cl with receptor **1** (X = Br) in $CDCl_3$ at 25°C.

K, X= Br

first run: 10200 ± 1000

second run: 11300 ± 600

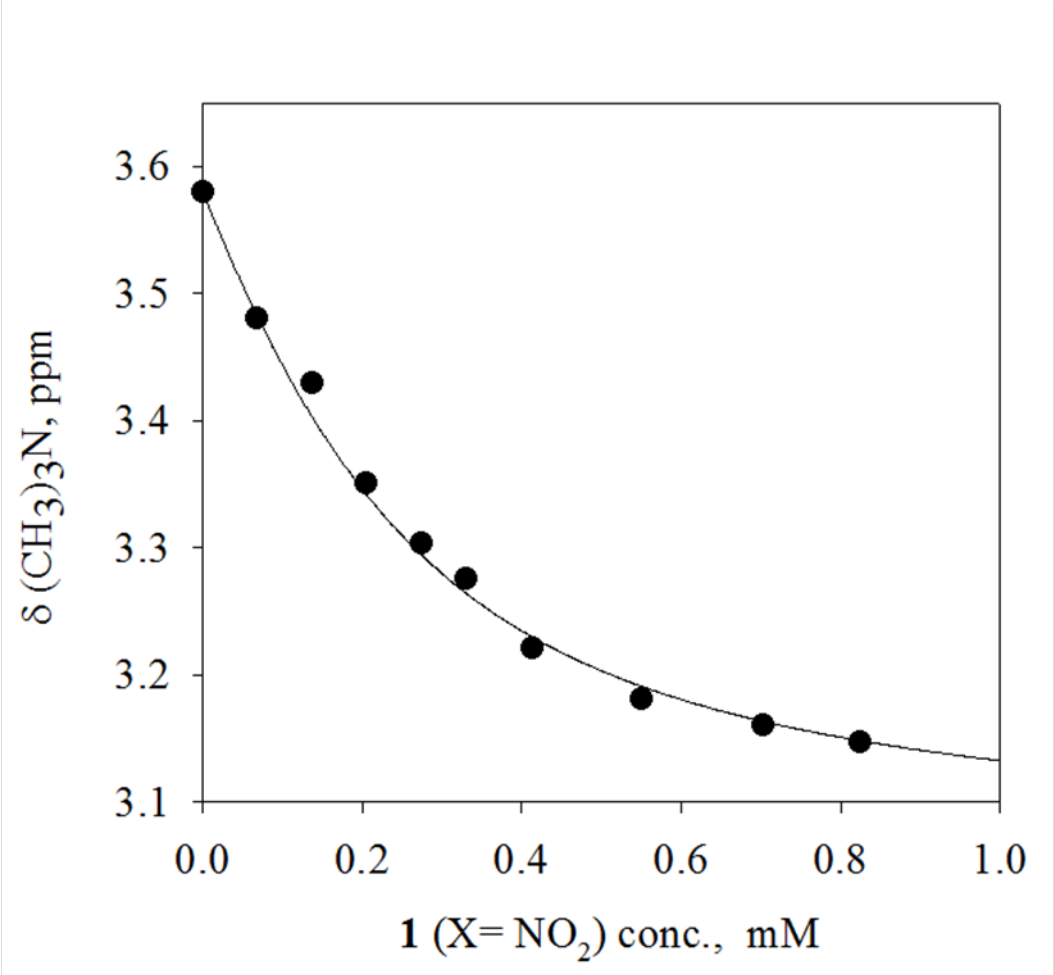

Figure 5S. ^{1}H NMR titration of 0.23 mM (TMA)Cl with receptor **1** (X = NO_2) in $CDCl_3$ at 25°C.

K, X= NO_2

first run: 6500 ± 1000

second run: 8550 ± 600