

Electronic Supplementary Information (ESI)

1) Matrix

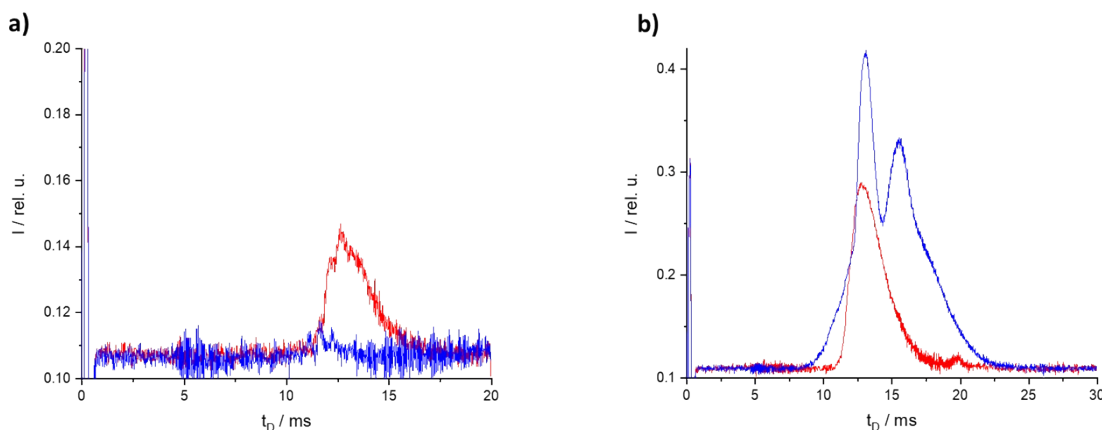


Fig. S.1 Matrix M1 (diesel – red) an M2 (petrol – blue) @355nm in IMS a) 1:100 in hexane and b) neat

2) Marker synthesis

Synthesis of N^1, N^1, N^5, N^5 -tetraethyl-naphthalene-1,5-diamine:

In a three neck flask 1,4-Diaminonaphthaline (1 equiv., 10 mmol, 1.59 g) and Ethyl bromide (8 equiv., 80 mmol, 8.72 g, 5.92 ml) are solved in abs. acetonitrile (75 mL) under argon atmosphere. After dry N,N-Diisopropylethylamine (8 equiv., 80 mmol, 10.32 g, 13.57 mL) was added drop wise at room temperature, the solution was stirred vigorously under reflux for 12 h. The reaction mixture were tested for complete consumption of the starting material by TLC. In the cause of unreacted staring material additional N,N-Diisopropylethylamine (3 equiv., 30 mmol, 3.87 g, 5.08 mL) and Ethyl bromide (3 equiv., 30 mmol, 3.27 g, 2.22 mL) were added and the reaction was stirred under reflux for additional 24 h. After complete conversion of the starting material, the reaction was cooled to room temperature and transferred to a separating funnel. After adding water and extraction with toluene (50 mL, three times), the organic layer was collected and dried over MgSO₄. The solvent was removed under reduced pressure and the resulting residue was purified by flash column chromatography using Hexane/Ethyl acetate = 50:1 as the mobile phase.

3) Marker selection

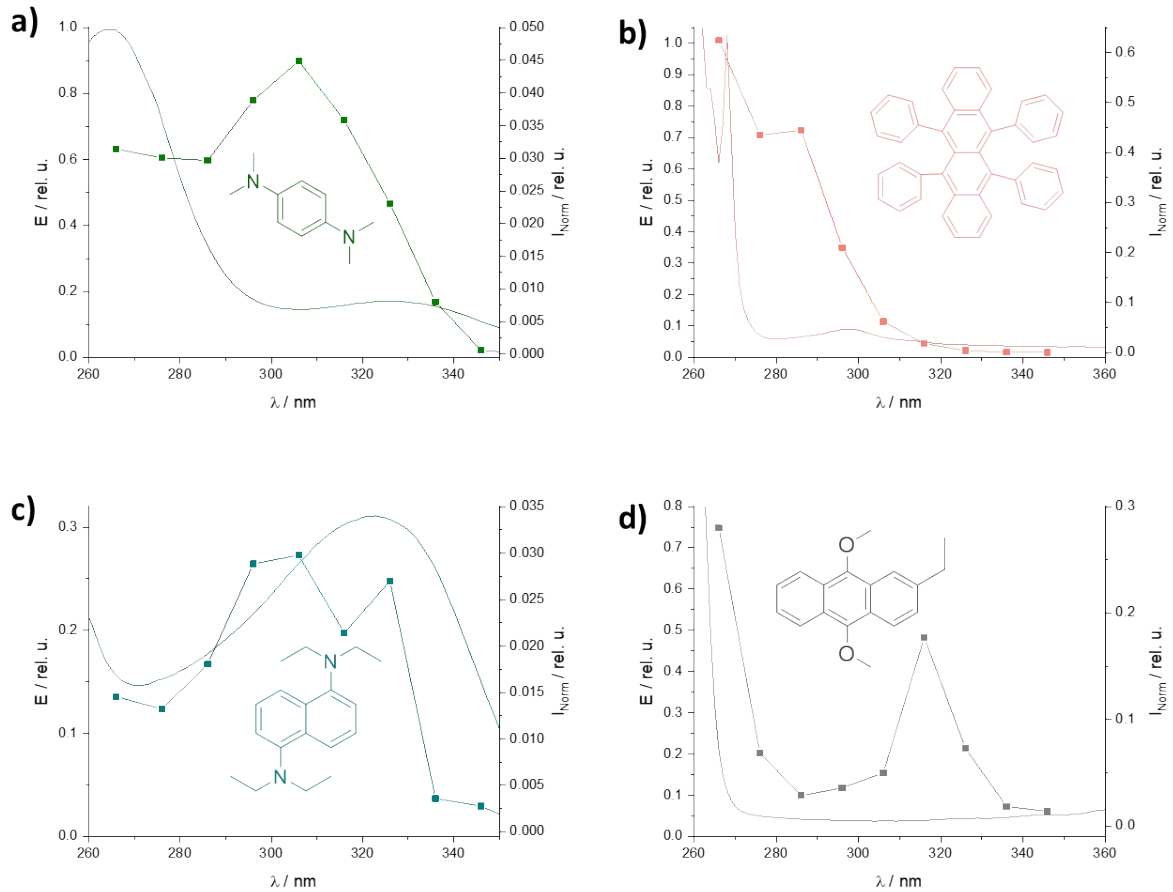


Fig. S.2 Marker at different wavelength, solid line = UV spectrum, dotted line = REMPI-MS for high tax [a) and c)] and low tax [b) and d)] marking, chemical structure in the graph, all in hexane, UV-VIS: quartz cuvettes (layer thickness 1 cm) with Lambda 750, Perkin Elmer, Waltham, USA).

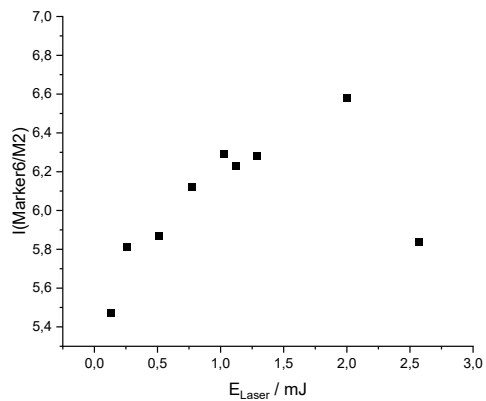


Fig. S.3 Marker-to-Matrix (TMPPD-to-M2) ratio over different pulse energies @355nm in MS

4)

5) Analytical performance

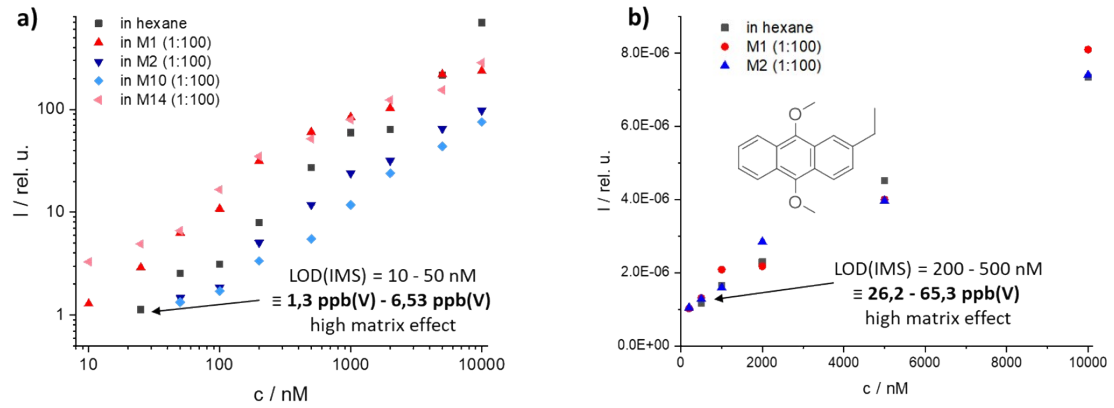


Fig. S.4 Signal intensity of Marker EDMA in hexane and diluted matrix at 355nm in a) MS and b) IMS

6) Charge transfer reaction

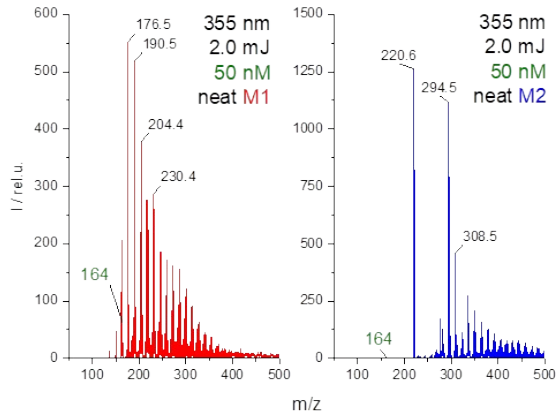


Fig. S.5 MS-spectra of diesel (red) and petrol (blue) with small amount of TMPPD (50 nM) for identification of highest peaks in matrix for strong CTRs in the presence of TMPPD