Separation, Characterisation and Estimation of Benzopyrene in Various Sources and Preparation of Water Soluble Benzopyrene-Metal Based Complexes

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Sanction Number: **MRP(S)-0502/13-14/KAMA002/UGC-SWRO**

Executive Summary

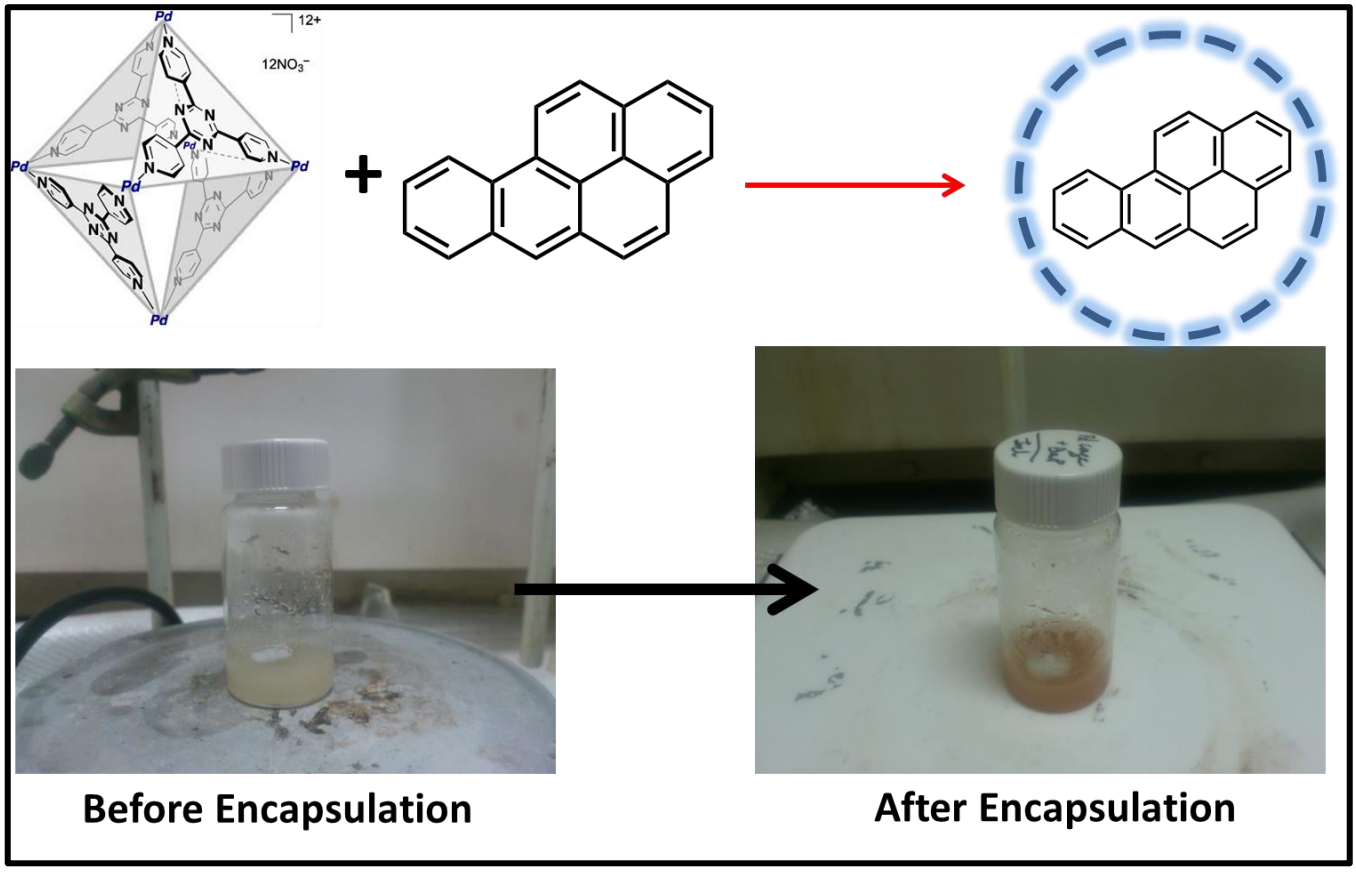
Benzo[a]pyrene and benzo[e]pyrene are polynuclear aromatic hydrocarbons formed due to the incomplete combustion of wood, cigarettes and fossil fuels. Benzo[a]pyrene is a well known carcinogen. It's presence in cigarette smoke and subsequent accumulation in the lungs has been found to be one of the main causes for lung cancer in smokers. Once this compound enters the body, it gets oxidised by cytochrome enzymes to its diol-epoxide, which is the ultimate carcinogen.

The project had primarily two objectives: one was to estimate the amount of benzo[a]pyrene (BaP) produced by the burning of various brands of cigarettes. The other objective was to make water soluble complexes of metals with BaP. To achieve the first, the high fluorescence quantum yield of BaP (0.3-0.4) made fluorimetry a sensitive and accurate method for estimation. 100 cigarettes were burnt, and the smoke was passed over Ambelite XAD-2 resin. The resin was sonicated in toluene for desorption of the adsorbed compounds and the extract was collected. Using synchronous fluorimetry, quantity of BaP in this sonicated extract could be found. The concentration of BaP in GFB (Gold Flake Blue – Lights^{TM}) was found to be 10.56ppb, extract from KR cigarettes (Gold Flake Kings^{TM}) gave a BaP concentration of 41.56ppb and NC (Navy Cut^{TM}) extract had a BaP content of 40.27ppb. Electrospray Ionisation Mass spectrometry (ESI-MS) on each the cigarette extracts gave a peak at m/z=253, corresponding to $[BaP+H]^+$ ion, further confirming the presence of BaP in the extracts.

To achieve the second objective i.e complexation, an encapsulation approach was thought of. This idea proved more favourable, as BaP being a compound with no ligating atoms does not form stable coordinate covalent bonds with most metal ions. For encapsulation, an octahedral Pd_6L_4 nanocage was used. This nanocage, has a cavity size about 2nm, and is made of 6 Pd^{+2} ions situated at the vertices of an octahedron and the alternating walls of the octahedron are occupied 2,4,6-trispyridyl-1,3,5-triazine (TPT) ligands. The cavity formed was able accumulate (encapsulate) the hydrophobic guest i.e BaP. The TPT ligands stabilised the BaP guest due to pi-pi stacking interactions. Furthermore, an aqueous mixture of BaP and the nanocage turned red, due to a charge transfer interaction between the TPT walls and the encapsulated BaP.

NMR spectroscopy on the BaP-nanocage mixture gave only the peaks of the nanocage. This was due to the low occupancy of BaP in the nanocage which was below the NMR detection limit. Surface Enhanced Raman Spectroscopy on the mixture showed a 17cm^{-1} shift of the C=C peak from 1605cm^{-1} to 1622cm^{-1}, this blue shift was caused due to a change in the electronic cloud of BaP due to encapsulation.

To conclude, both objectives of the project were achieved. Estimation of BaP in cigarettes proved easier by synchronous fluorimetry as it did not require a separation procedure. The encapsulation approach was advantageous as the reaction could be done in the aqueous medium.



Above: The scheme for encapsulation of the BaP. The nanocage with Pd^{+2} ions and TPT walls is shown and represented with the dashed circle on the right side. Note the red colour of the mixture after encapsulation.

Acknowledgements: J.C would like to thank Darren Christie, Mamatha N and Ranjana K for help with the project. The staff of UG and PG Departments of Chemistry, St Aloysius College for their suggestions and support. Dr Jyotishman Dasgupta and Ms Ankita Das of TIFR Mumbai for help with the encapsulation approach for BaP complexation and Raman Facilities. Dr Ankona Datta and Ms Ananya Rakshit of TIFR, Mumbai for the ESI-MS facility. Mr Shantanu Aggarwal of JNCASR, Bangalore for the silver nanoparticles.