Amination and Trifluoroethylation of Fullerenes Promoted by Subphthalocyanine Capsules

Significance: A dimeric subphthalocyanine (Sub-Pc) capsule (\textit{SubPc}_2\textit{Pd}_3) promoted the amination of C_{60} fullerene with aromatic (trimethylsilyl)amines in H_2O/CH_2Cl_2 and the trifluoroethylation with CF_3CH_2I in CH_2Cl_2 under green-light irradiation to give the corresponding products in up to 86% yield (eqs. 1 and 2).

Comment: \textit{SubPc}_2\textit{Pd}_3 was prepared according to a previously reported method (\textit{J. Am. Chem. Soc.} 2013, 135, 10503). It showed a much higher activity than monomeric SubPc in both reactions, indicating that the formation of host–guest complexes between \textit{SubPc}_2\textit{Pd}_3 and the fullerene accelerates the reactions.

\textbf{Results:}

\begin{align*}
\text{(1)} & \quad \text{H}_2\text{O–CH}_2\text{Cl}_2 (1\%) \quad 530 \text{ nm LED, 6 h, r.t., Ar} \\
\text{SubPc}_2\textit{Pd}_3 (1.0 \text{ equiv}) + & \quad \text{R}_1\text{N}\text{TMS} \quad (1.5 \text{ equiv}) \\
\quad & \quad \rightarrow \text{H} \quad \text{R}_1^2 \quad \text{TMS} \\
\text{R} = \text{H}, 86\% \text{ yield} & \quad \text{R} = \text{Me}, 71\% \text{ yield} \\
\text{R} = \text{Br}, 74\% \text{ yield} & \quad \text{R} = \text{OMe}, 68\% \text{ yield} \\
\end{align*}

\begin{align*}
\text{(2)} & \quad \text{CH}_2\text{Cl}_2 \quad 530 \text{ nm LED} \quad 6 \text{ h, r.t., Ar} \\
\text{SubPc}_2\textit{Pd}_3 (1.0 \text{ equiv}) + & \quad \text{F}_3\text{CH}_2\text{I} \quad (1.5 \text{ equiv}) \\
\quad & \quad \rightarrow \text{CF}_3 \quad \text{H} \\
\text{65\% yield} & \quad \text{52\% yield} \\
\end{align*}