Microwave-assisted synthesis, photophysical and electrochemical properties of thermal-stable naphthalene benzimidazoles and naphthalimides are studied in this paper. Microwave-assisted synthesis of naphthalene benzimidazoles provide higher yields than the conventional thermal synthesis. Comparative photophysical properties of naphthalene benzimidazoles and naphthalimides are revealed that conjugation of electron-donating group onto naphthalimide moiety increases fluorescence quantum yields. Fluorophore-solvent interactions are also investigated using Lippert-Mataga equation for naphthalimides and naphthalene benzimidazoles. Thermal stabilities of naphthalene benzimidazoles are better than naphthalimides due to increased aromaticity. The experimental $E_{\text{LUMO}}$ levels of naphthalene benzimidazoles are found to be between 3.15 and 3.28 eV. Therefore, naphthalene benzimidazole derivatives consisting of anchoring groups are promising materials in organic dye sensitized solar cells.