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Azobenzene-functionalized poly(alkyl aryl ether) dendrimers of several generations are synthesized and studies for their photochemical and photophysical properties in solution and as thin films. The photochemical behavior of the azodendrimers in solution indicates that the azobenzene units behave independently, very similar to the constituent monomer azobenzene unit, the properties of thin solid films of the dendrimers are distinctly different. The azodendrimers, AzoG1, AzoG2 and AzoG3 are observed to form stable supercooled glasses, which showed long wavelength absorption and red emission characteristic of J-aggregates of the azobenzene chromophores. Reversibility of the photoinduced isomerization of the azodendrimers in the glassy state is described.