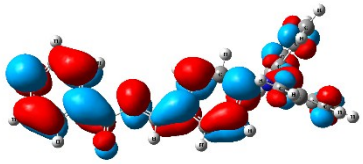
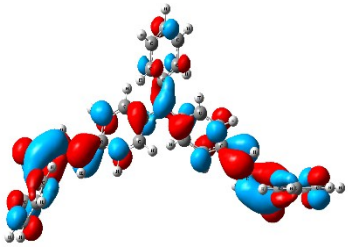
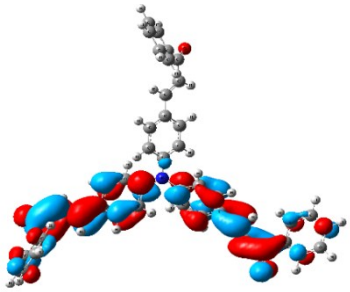
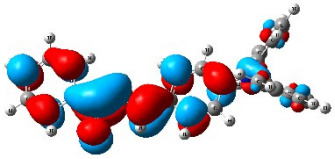
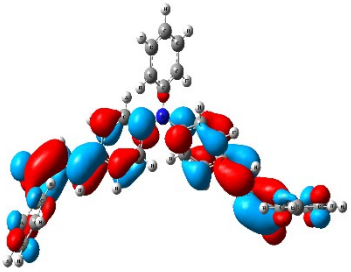
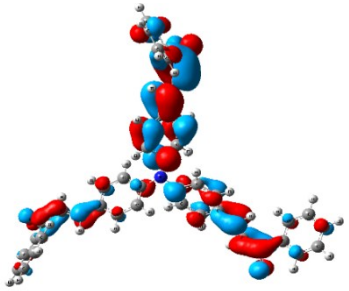
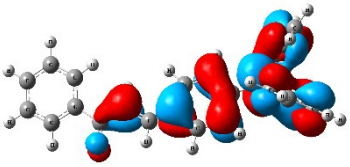
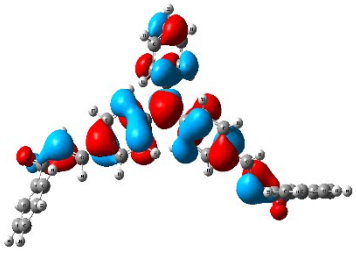
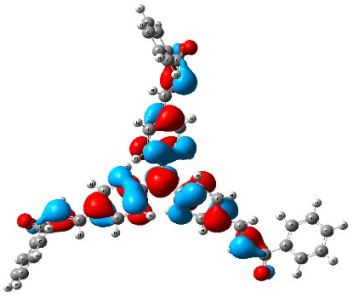
Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

SUPPLEMENTARY INFORMATION

Triphenylamine based Donor – π – Acceptor Organic Phosphors: Synthesis, Characterization and Theoretical study

Aravind Babu Kajjam, Santanb Giri and Sivakumar V.*

Department of Chemistry, National Institute of Technology, Rourkela, 769008, India.

Frontier Orbitals	FTPA	DFTPA	TFTPA
LUMO+1			
LUMO			
HOMO			

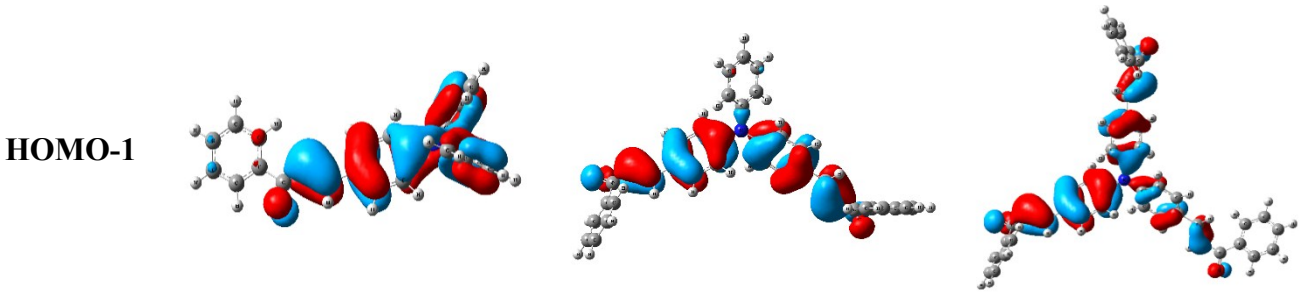


Fig.S1. HOMO, LUMO energy diagrams of FTPA, DFTPA, TFTPA-Acetophenone phosphors.

ST1: Computed Vertical Transitions and Their Oscillator Strengths and Configurations[a]

Compound	State	λ_{max} nm	*f*	Configuration
FTPA-Acetophenone	Gas	423.36	0.7624	HOMO → LUMO (70.2%)
		305.71	0.1575	HOMO → LUMO+2 (23.13%)
				HOMO → LUMO+3 (65.74%)
		300.87	0.2596	HOMO → LUMO+1 (48.97%)
				HOMO → LUMO+2 (43.26%)
		293.35	0.2514	HOMO-3 → LUMO (12.18%)
				HOMO-2 → LUMO (59.24%)
	Toluene	448.91	0.8767	HOMO → LUMO (70.3%)
		306.69	0.2686	HOMO → LUMO+1 (48.96%)
		305.83	0.292	HOMO → LUMO+1 (31.57%)
				HOMO → LUMO+3 (59.65%)
		301.89	0.2017	HOMO-1 → LUMO (60.10%)
				HOMO → LUMO+1 (24.76%)
	THF	456.58	0.8502	HOMO → LUMO (70.34%)
		30.862	0.4076	HOMO → LUMO+1 (54.16%)
		304.26	0.2678	HOMO-1 → LUMO (46.83%)
				HOMO → LUMO+1 (24.08%)
	DCM	457.85	0.8531	HOMO → LUMO (70.35%)
		308.92	0.4172	HOMO-1 → LUMO+1 (53.40%)
		304.55	0.1963	HOMO-1 → LUMO (55.39%)
				HOMO → LUMO+1 (32.09%)
		303.95	0.1474	HOMO-1 → LUMO (15.8%)
				HOMO → LUMO+1 (13.18%)
				HOMO → LUMO+3 (66.22%)
	Chloroform	454.59	0.8605	HOMO → LUMO (70.33%)

		308.04	0.3818	HOMO → LUMO+1 (55.7%)
		304.71	0.2521	HOMO → LUMO+2 (12.45%)
				HOMO → LUMO+3 (67.54%)
		303.55	0.1286	HOMO-1 → LUMO (58.3%)
				HOMO → LUMO+1 (31.11%)
	Acetonitrile	459.48	0.8345	HOMO → LUMO (70.36%)
		309.54	0.4414	HOMO → LUMO+1 (51.13%)
		304.9	0.1210	HOMO-1 → LUMO (55.69%)
				HOMO → LUMO+1 (37.27%)
		303.09	0.1882	HOMO → LUMO+2 (10.35%)
				HOMO → LUMO+3 (68.63%)
DFTPA-Acetophenone	Gas	433.06	0.69756	HOMO → LUMO (70.29%)
		390.16	0.227	HOMO → LUMO (69.49%)
		299.6	0.2813	HOMO-2 → LUMO+1 (18.7%)
				HOMO-1 → LUMO (47.3%)
				HOMO → LUMO+3 (12.31%)
		294.01	0.1492	HOMO → LUMO+5 (14.5%)
				HOMO-6 → LUMO (14.38%)
	DCM	459.03	1.0711	HOMO → LUMO (7.31%)
		408.32	0.2736	HOMO → LUMO+1 (69.69%)
		305.25	0.3429	HOMO-1 → LUMO (35.21%)
				HOMO → LUMO+3 (41.75%)
				HOMO → LUMO+5 (12.12%)
				HOMO → LUMO+7 (12.49%)
		295.14	0.3618	HOMO-9 → LUMO+1 (1086%)
				HOMO-8 → LUMO (16.2%)
				HOMO-2 → LUMO (20.05%)
TFTPA-Acetophenone	Gas	435.06	0.7929	HOMO → LUMO (70.22%)
		434.54	0.7957	HOMO → LUMO+1 (70.23%)
		305.85	0.3364	HOMO-5 → LUMO+1 (18.91%)
				HOMO-3 → LUMO (26.06%)
				HOMO-2 → LUMO (37.53%)
		305.76	0.3430	HOMO-4 → LUMO (10.16%)
				HOMO-2 → LUMO+1 (44.97%)
				HOMO-1 → LUMO+1 (27.6%)
	DCM	456.35	0.8909	HOMO → LUMO (46.48%)

				HOMO → LUMO+1 (52.75%)
		456.23	0.8955	HOMO → LUMO (52.75%)
		309.58	0.4439	HOMO-5 → LUMO+1 (12.62%)
				HOMO-4 → LUMO (11.72%)
				HOMO-4 → LUMO+1 (10.76%)
				HOMO-3 → LUMO+1 (13.71%)
				HOMO-2 → LUMO (35.77%)
				HOMO-2 → LUMO+1 (24.75%)
				HOMO-1 → LUMO (25.60%)
		309.47	0.4060	HOMO-4 → LUMO+1 (12.56%)
				HOMO-3 → LUMO (12.59%)
				HOMO-2 → LUMO+1 (33.17%)
				HOMO-1 → LUMO (33.19%)
				HOMO-1 → LUMO+1 (25.01%)

[a]Orbital contributions below 10% are omitted

Solvatochromism studies:

The fluorescence excitation and emission spectra of yellow phosphors in different polar and non-polar solvents are given in Fig. 1a, 1 b and 1 c, respectively. It is clearly demonstrates that the significant solvent dependent shifts was observed in the emission maxima. Table ST2, summarizes the absorption maxima, emission maxima and Stoke's shift of all the yellow phosphors. However, solvent polarity exerts a great effect on their PL emission. With the increase of the solvent polarity gradually, the PL spectrum of each compound is progressively shifted to a longer wavelength. The emission peaks of FTPA-, DFTPA- and TFTPA-Acetophenone are 484, 482 and 480 nm in toluene and 582, 545 and 544 nm in DMF. Compared with the emission peak in a toluene solution, the peak positions in DMF are red-shifted by 98, 63 and 64 nm for FTPA-, DFTPA- and TFTPA-Acetophenone, respectively. Solvent-dependent spectral shifts are often interpreted in terms of the Lippert−Mataga equation (eq-1), which describes the solvatochromic Stokes shift Δf (expressed in wavenumbers) as a function of the change of the dipole moment $\Delta\mu ge = \mu e - \mu g$ of the phosphor material upon excitation. The validity of equation-1 can be checked by using various solvents with different dielectric constants (ε) and refractive indices (n) and by plotting stokes shift verses Δf for the 7 solvents. .[1,2]

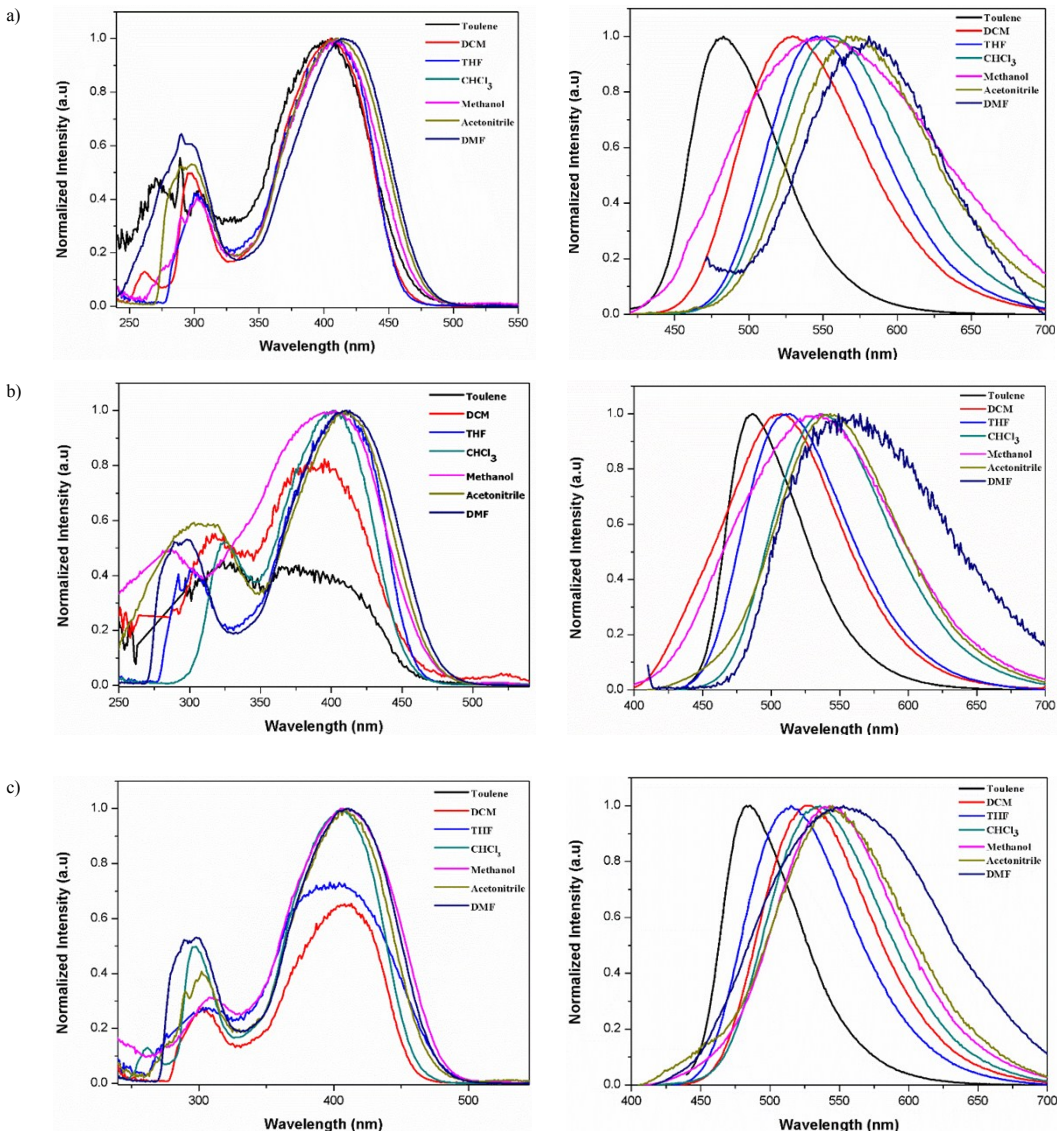


Fig.1a). Normalized excitation and emission spectra of FTPA-Acetophenone in solvents of different polarity. Figure 1b). Normalized excitation and emission spectra of DFTPA-Acetophenone in solvents of different polarity. Figure 1c). Normalized excitation and emission spectra of TFTPA-Acetophenone in solvents of different polarity.

$$\Delta V = \frac{2\Delta f}{4\pi\epsilon_0 hca^3}(\mu_e - \mu_g) + \text{Constant} \quad \text{..... eq.1}$$

$$f(\epsilon) = \frac{f(\epsilon - 1)}{f(2\epsilon + 1)} \quad \text{and} \quad f(n^2) = \frac{(n^2 - 1)}{(2n^2 + 1)} \quad \text{..... eq.2}$$

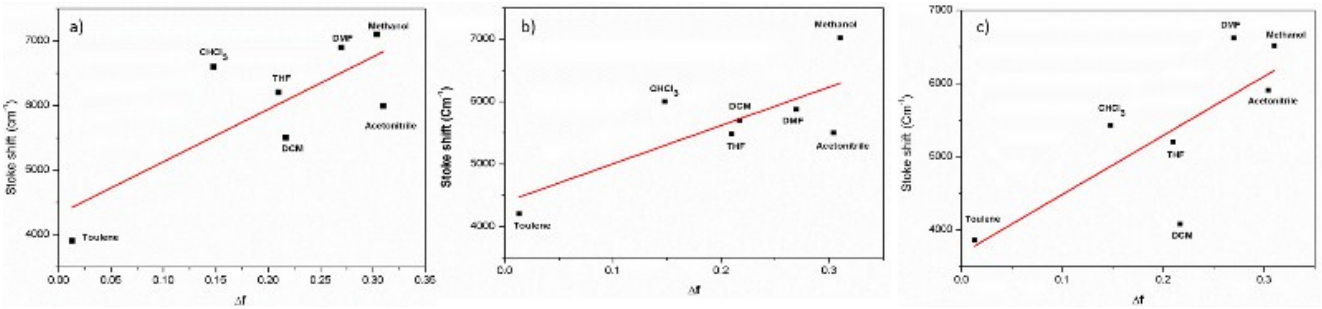


Fig.2 a). Stokes shift Δf of FTPA-Acetophenone versus the Lippert solvent parameter Δf = f(ε) – f(n2). The straight line represents the best linear fit to the 7 data points. Fig.2b). Stokes shift Δf of DFTPA-Acetophenone versus the Lippert solvent parameter Δf = f(ε) – f(n2). The straight line represents the best linear fit to the 7 data points. Fig.2c). Stokes shift Δf of TFTPA-Acetophenone versus the Lippert solvent parameter Δf = f(ε) – f(n2). The straight line represents the best linear fit to the 7 data points.

Fig 2a represents the Lippert−Mataga plot for FTPA-Acetophenone in different solvents which is mentioned in the supplementary information (ST2). As is evident from Figure, there is a good linear relationship [correlation coefficient r = 0.529, slope = (8.128) × 10^3 cm^{-1}, intercept = (4.31) × 10^3 cm^{-1}] of the Stokes shift plotting Δν verses Δf for the 7 solvents. Similarly, Figure 13b and 13c represents the Lippert−Mataga plot for DFTPA-Acetophenone and TFTPA-Acetophenone in different solvents (ST3). As is evident from Figure 13b, there is a good linear relationship [correlation coefficient r = 0.5038, slope = (6.15) × 10^3 cm^{-1}, intercept = (4.38) × 10^3 cm^{-1}] of the plotting Stokes shift Δν verses Δf for the 7 solvents. Similarly in the case of TFTPA-Acetophenone, as is apparent from Figure. 13c, there is a good linear relationship [correlation coefficient r = 0.5115, slope = (6.15) × 10^3 cm^{-1}, intercept = (3.67) × 10^3 cm^{-1}] of the Stokes shift. The graph plotting stokes shift Δν verses Δf for the 7 solvents.

ST 2: Photoluminescence spectral data of various solvents of yellow phosphors

Solvent	λ_{abs} (max) (nm)			λ_{em} (max) (nm)			Stoke's shift (Δν) (cm^{-1})		
	FTPA	DFTPA	TFTPA	FTPA	DFTPA	TFTPA	FTPA	DFTPA	TFTPA
Toulene	408	401	405	484	482	480	3900	4200	3860
$CHCl_3$	409	406	409	555	537	526	6600	6000	5430
THF	406	397	405	543	514	513	6200	5480	5200
DCM	409	395	400	528	513	490	5500	5700	4080

DMF	416	413	408	582	545	544	6900	5873	6620
Acetonitrile	405	409	406	571	535	534	7100	5500	5910
Methanol	415	402	407	557	560	554	6190	7020	6520

ST3. CIE color coordinates of all phosphors in different solvents.

Solvent	**FTPA-Acetophenone**		**DFTPA-Acetophenone**		**TFTPA-Acetophenone**	
	x	**y**	**x**	**y**	**x**	**y**
Toulene	0.1500	0.3396	0.1657	0.514	0.1617	0.5060
DCM	0.2436	0.5367	0.2853	0.5029	0.2877	0.4668
THF	0.3838	0.5720	0.2564	0.5509	0.2630	0.5587
$CHCl_3$	0.4194	0.5484	0.3557	0.5714	0.3413	0.5665
Methanol	0.3864	0.4861	0.3120	0.4555	0.3618	0.5407
Acetonitrile	0.4608	0.5150	0.3618	0.5407	0.3662	0.5187
DMF	0.4862	0.5051	0.4254	0.5278	0.3923	0.4970

Reference:

1 V. E. Lippert, A: *Phys. Sci.,* 1955, 10, 541−545.

2 (a) N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn*., 1955, 28, 690−691.

(b) N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.,* 1956, 29, 465−470.