Supplementary Information

Development and demonstration of highly potent flame-retardant cotton fabric.

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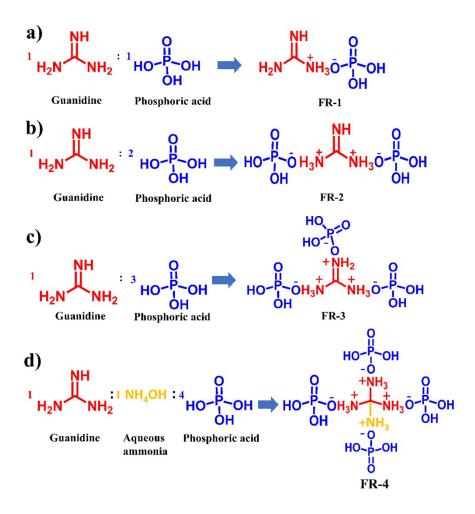


Figure S1. Synthesis and chemical structure of a) FR-1, b) FR-2, c) FR-3, and d) FR-4 composite.

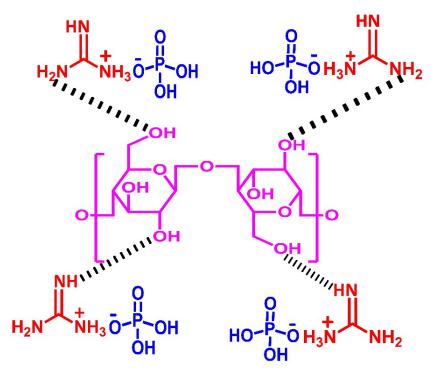


Figure S2: Ionic interaction of FR-1 composite with cotton fabric (FR-1@cotton fabric).

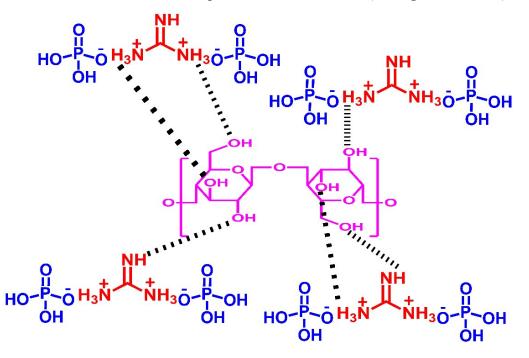


Figure S3: Ionic interaction of FR-2 composite with cotton fabric (FR-2@cotton fabric).

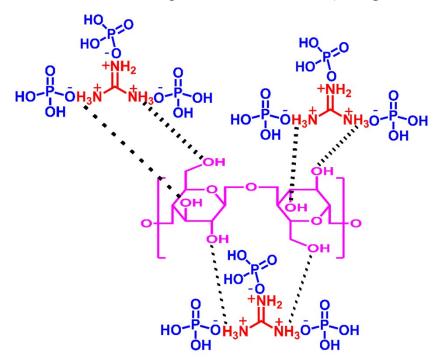


Figure S4: Ionic interaction of FR-3 composite with cotton fabric (FR-3@cotton fabric).

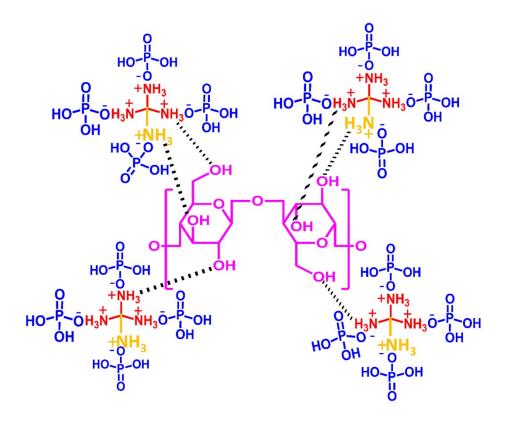


Figure S5: Ionic interaction of FR-4 composite with cotton fabric (FR-4@cotton fabric).

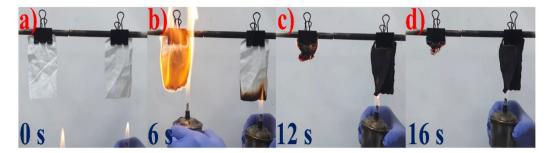


Figure S6: Digital photograph of the flame-retardant test of control cotton fabric coated with a-d) guanidine hydrochloride.

In **Figure S6** the guanidine hydrochloride coated cotton fabric catches fire and sustains up to 16 s it may be because of presence of nitrogen functionality. Meanwhile, the control cotton fabric, shrinkage was observed and after flame test, the fabric losses its strength and become brittle. Whereas the blank cotton fabric was burn completely within 14 s.

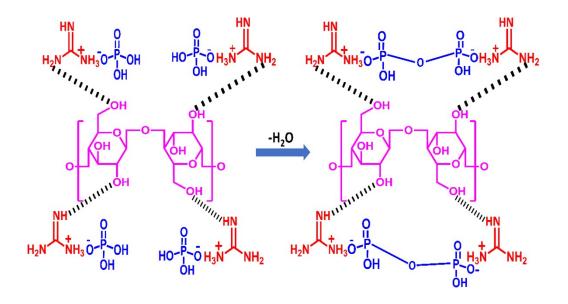


Figure S7: Schematic representation for the proposed dehydration of the FR-1 by forming phosphoanhydride by intramolecular as well as intermolecular reaction.

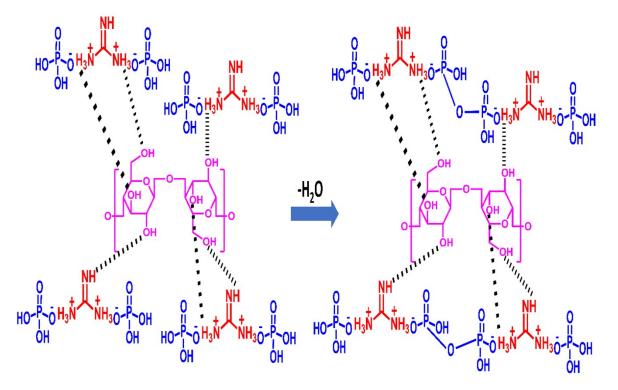


Figure S8: Schematic representation for the proposed dehydration of the FR-2 by forming phosphoanhydride by intramolecular as well as intermolecular reaction.

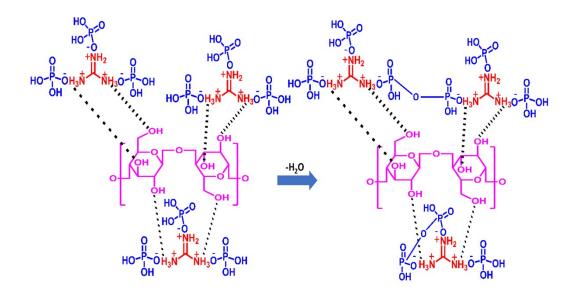


Figure S9: Schematic representation for the proposed dehydration of the FR-3 by forming phosphoanhydride by intramolecular as well as intermolecular reaction.

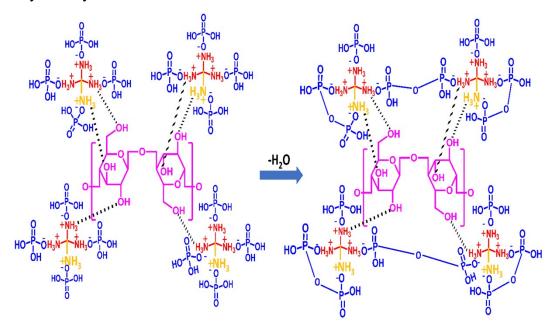


Figure S10: Schematic representation for the proposed dehydration of the FR-4 by forming phosphoanhydride by intramolecular as well as intermolecular reaction.

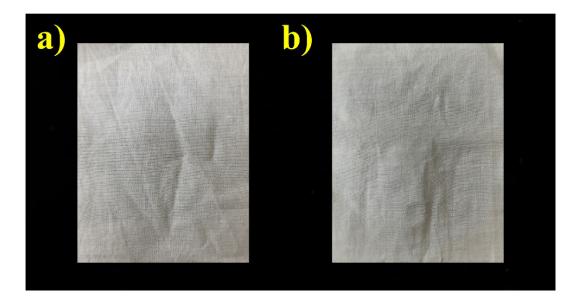


Figure S11. Digital photograph of (a) Blank sample, (b) FR-4@cotton fabric

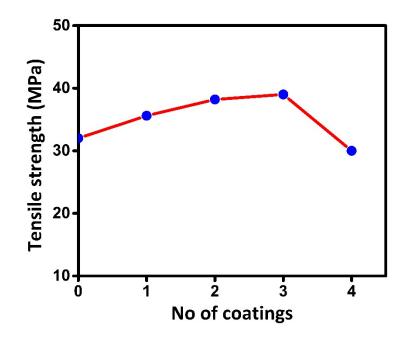


Figure S12. Tensile strength of FR-4@Cotton fabric

The durability of FR-4@Cotton fabric, we examined with tensile strength test. The tensile strength of FR-4@Cotton fabric was measured by using reported method in which we observed that the trend of tensile strength of FR-4@Cotton fabric was increased. The maximum tensile strength was observed of FR-4@Cotton fabric for 3rd no of coating and after that the tensile strength of FR-4@Cotton was gradual decreased. The tensile strength results of FR-4@Cotton fabric is summarized in **Figure S12**.

Table S1: The Weight % and stochiometric feed ratio of carbon, oxygen, nitrogen and phosphorous of FR-1 to FR-4 material based on XPS data

Sr.	Name of	Carbon		Oxygen		Nitrogen		Phosphorous	
No.	FR	Weight	Stochiometric	Weight	Stochiometric	Weight	Stochiometric	Weight	Stochiometric
	Composite	%	ratio	%	ratio	%	ratio	%	ratio
	material								
1	FR-1	12	0.99 (~1)	44	3.82 (~4)	32	2.89 (~3)	12	0.99 (~1)
2	FR-2	9	0.85 (~1)	56	7.92 (~8)	21	2.84 (~3)	14	1.89 (~2)
3	FR-3	8	0.78 (~1)	60	11.95 (~12)	16	2.85 (~3)	16	2.95 (~3)
4	FR-4	6	0.77 (~1)	64	16.02 (~16)	15	3.78 (~4)	15	3.85 (~4)

Table No. S2: LOI (%) value of synthesized material coated cotton fabric with respect to no of coating.

No of coating	Guanidine + PA (1:1)Guanidine + PA (1:2)(FR-1@cotton(FR-2@cotton)		Guanidine + PA (1:3) (FR-3@cotton	Guanidine + NH ₄ OH + PA (1:1:4) (FR-4@cotton fabric)
	fabric)	fabric)	fabric)	
1 st Coating	35	40	48	50
2 nd Coating	37	42	50	52
3 rd Coating	40	46	51	53
4 th Coating	43	48	53	55

*The LOI of blank cotton fabric was 16%.

Sr.	Flame retardant material	LOI	Reference
No.		10.0	
1.	Thiourea, phosphoric acid, PCl ₅ ,	48.2	[1]
	ethanolamine, urea		
2.	Formaldehyde, melamine, anhydrous	43.0	[2]
	H_3PO_3 , urea		
3.	alkylammonium func-	29	[3]
	tional silsesquioxane, phytic acid		
4.	Glycerol, phosphoric acid, urea	33.7	[4]
5.	Diethyl chlorophosphite, Methacrylamide,	30.2	[5]
	Triethylamine		
6.	Casein, dimethyl phosphite, formaldehyde,		
	phosphoric acid (H ₃ PO ₃)	41.6	[6]
7.	Guanidine, phosphoric acid (FR-1)	43	This Work
8.	Guanidine, phosphoric acid (FR-2)	48	This Work
9.	Guanidine, phosphoric acid (FR-3)	53	This Work
10.	Guanidine hydrochloride, ammonium		
	hydroxide, Phosphoric acid (FR-4)	55	This Work

Table No. S4: Vertical flammability data of control cotton fabric with flame retardant material coated cotton fabric.

Flammability parameter	Blank Cotton	Guanidine + PA (1:1)	Guanidine + PA (1:2)	Guanidine + PA (1:3)	Guanidine + NH ₄ OH + PA (1-1-4)
	fabric	(FR-1@cotton fabric)	(FR-2@cotton fabric)	(FR-3@cotton fabric)	(1:1:4) (FR-4@cotton fabric)
Occurring					(111 (@00000 10010)
flashing over the	Yes	No	No	0	0
surface					
Burning with					
flame time (s)	17	0	0	0	0
Burning with					
afterglow time					
(s)	0	0	0	0	0
After flame stop					
Total burning					
time (s) (Flame					
time + after	17	0	0	0	0
glow time)					
Char length	Nil	5	4	3.5	3
(cm)					

Table No S5: Comparative data of as synthesized material with respect to LOI, VFT and observation observed in spirit lamp test.

Sr.	FR material	Composition	LOI	VFT	Observation observed in Spirit
No.			(%)	(cm)	lamp test
1.	FR-1@cotton fabric	Guanidine + Phosphoric acid (1:1)	43	5	Acted as a good FR material but shrink the cotton fabric and sustained up to 327 s.
2.	FR-2@cotton fabric	Guanidine + Phosphoric acid (1:2)	48	4	Improved FR efficiency and performed effective FR material but shrink the cotton fabric and sustained up to 424 s.
3.	FR-3@cotton fabric	Guanidine + Phosphoric acid (1:3)	53	3.5	Improved FR efficiency and performed efficient FR material but shrink the cotton fabric and sustained up to 470 s.
4.	FR-4@cotton fabric	Guanidine + ammonium hydroxide Phosphoric acid (1:1)	55	3	Improved FR efficiency and performed as a highly effective FR material without changing its initial shape and sustain up to 492 s.

Table S6: Wash fastness Data of FR-4@Cotton fabric without and with Binder/FR-4@Cotton fabric before and after washing % weight loss

		Before Washing			After 1 st Washing			
Sr.	Sample							% weight
No.								loss
		Weight	LOI	Char	Weight	LOI	Char	
		(gm)	(%)	length	(gm)	(%)	length	
				(cm)			(cm)	
1	FR-4@Cotton	1.1006	55	3	0.7526	45.5	5	31.61
	Fabric							
2	Binder/FR-	1.1021	54.5	3.2	0.9695	52.1	3.6	12.03
	4@Cotton							
	Fabric							

The wash fastness data of synthesized FR-4@Cotton fabric was tested by ISO2 method.²⁹ FR-4@Cotton fabric was washed with 5 g/L of soap solution with liquor ratio 50:1 at 50 °C for 45 min, after rinsed properly with water and dried it in air. We observed maximum ~31.61 % weight loss in case of FR-4@Cotton fabric after washing. Whereas, only ~12.03 % of weight loss is observed, by using Saraprint AC as a binder.²⁹

Table No S7: Add on % data of FR-1 material on cotton fabric

Sr. No.	Weight of cotton fabric (g)	No. of coatings	Weight FR- 1@cotton cloth (g)	FR-1 Load (%)	Results after exposure to similar flame (Spirit lamp test)
1.	0.640	1 st Coating	0.743	~16	Served as a moderate FR material towards cotton fabric.
1.	0.040	Coating	0.745	~10	
2.	0.638	2 nd Coating	0.759	~19	Improved FR efficiency and showed good FR performance towards cotton fabric.
3.	0.638	3 rd Coating	0.781	~22	Improved FR efficiency and performed effective FR performance towards the cotton fabric.
4.	0.639	4 th Coating	0.806	~26	Improved FR efficiency and performed excellent FR performance towards cotton fabric.

Table No S8: Add on % data of FR-2 material on cotton fabric

Sr. No.	Weight of cotton fabric (g)	No. of coatings	Weight FR- 2@cotton cloth (g)	FR-2 Load (%)	Results after exposure to similar flame (Spirit lamp test)
		1 st			Served as a good
1.	0.639	Coating	0.749	~17	FR material towards cotton fabric.
					Improved FR efficiency and showed
2.	0.640	2 nd	0.769	~20	effective FR performance towards cotton
		Coating			fabric.
					Improved FR efficiency and performed

3.	0.638	3 rd	0.785	~23	excellent FR performance towards the
		Coating			cotton fabric.
4.	0.636	4 th Coating	0.815	~28	Improved FR efficiency and performed outstanding FR performance towards cotton fabric.

Table No S9: Add on % data of FR-3 material on cotton fabric

Sr. No.	Weight of cotton	No. of coatings	Weight FR- 3@cotton	FR-3 Load	Results after exposure to similar flame (Spirit lamp test)
	fabric (g)		cloth (g)	(%)	
		1 st			Served as a effective
1.	0.639	Coating	0.755	~18	FR material towards cotton fabric.
					Improved FR efficiency and showed
2.	0.640	2 nd	0.781	~22	excellent FR performance towards cotton
		Coating			fabric.
					Improved FR efficiency and performed
3.	0.638	3 rd	0.798	~25	very effective FR performance towards
		Coating			the cotton fabric.
					Improved FR efficiency and performed
4.	0.638	4 th	0.832	~30	outstanding FR performance towards
		Coating			cotton fabric.

Table No S10: Add on % data of FR-4 material on cotton fabric

Sr. No.	Weight of cotton	No. of coatings	Weight FR- 4@cotton	FR-4 Load	Results after exposure to similar flame (Spirit lamp test)
	fabric (g)	0	cloth (g)	(%)	
1.	0.640	1 st	0.769	~20	Served as a excellent
		Coating			FR material towards cotton fabric.
2.	0.639	2 nd	0.794	~24	Improved FR efficiency and showed very
		Coating			effective FR performance towards cotton
					fabric.
3.	0.640	3 rd	0.827	~29	Improved FR efficiency and performed
		Coating			outstanding FR performance towards the
		_			cotton fabric.
4.	0.641	4 th	0.853	~33	Improved FR efficiency and performed
		Coating			magnificent FR performance towards
					cotton fabric.

 Table No. S11. Bending length and stiffness data of FR@Cotton fabric.

Sr. No.	Name of FR@Cotton	Whi	teness	Whiteness
	fabric	Warp	Weft	
1.	Control	1.5	1.4	127
2.	FR-1@Cotton fabric	1.7	1.6	128.159
3.	FR-2@Cotton fabric	1.8	1.7	131.884
4.	FR-3@Cotton fabric	1.9	1.8	132.074

5. FR-4@Cotton fabric	2.1	2.0	132.300
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References:

[1] Caiyan Wan, Mingsheng Liu, Pingping He, Guangxian Zhang, Fengxiu Zhang, A novel reactive flame retardant for cotton fabric based on a thiourea-phosphoric acid polymer, Industrial Crops & Products 154 (2020) 112625.

[2] Fengxiu Zhang, Weiwei Gao, Yaling Jia, Yi Lu, Guangxian Zhang, A concise water-solvent synthesis of highly effective, durable, and eco-friendly flame-retardant coating on cotton fabrics, Carbohydrate Polymers 199 (2018) 256–265

[3] Guo WW, Wang X, Huang JL, Zhou YF, Cai W, Wang JL, Song L, Hu Y (2020) Construction of durable flameretardant and robust superhydrophobic coatings on cotton fabrics for water-oil separation application, Chemical Engineering Journal 398 (2020) 125661.

[4] Jinfeng Li, Wei Jiang, Maolin Liu, Durable phosphorus/nitrogen flame retardant for cotton fabric, Cellulose (2022) 29:4725–4751.

[5] Ying Liu, Li Zhou, Fang Ding, Shanshan Li, Rong Li, Zhiguang Li, Dan Huang and Xuehong Ren, Flame-retardant cotton fabrics modified with phosphoramidate derivative via electron beam irradiation process, DOI: 10.1177/1528083719881816.

[6] Fang Xu. Guangxian Zhang. Peng Wang. Fangyin Dai, Durable and high-efficiency casein-derived phosphorusnitrogen-rich flame retardants for cotton fabrics, Cellulose (2022) 29:2681–2697.